

ENVIRONMENTAL RESEARCH

FATE OF VOLATILE ORGANIC COMPOUNDS IN WASTEWATER COLLECTION SYSTEMS

Volumes I - III

RAC Project No. 577G

MINISTRY OF ENVIRONMENT AND ENERGY

1

**FATE OF VOLATILE ORGANIC COMPOUNDS
IN WASTEWATER COLLECTION SYSTEMS**

Volumes I - III

RAC Project No. 577G

Report prepared by:

Principal Investigator: Richard L. Corsi¹
School of Engineering, University of Guelph

Co-Investigator: Gordon Hayward
School of Engineering, University of Guelph

Co-Investigator: John Bell
Enviromega Ltd and School of Engineering,
University of Guelph

Chris Quigley², Arlene Whitmore³, Michelle Swanston
School of Engineering, University of Guelph

¹ Now with the Department of Civil Engineering, The University of Texas at Austin, Austin, Texas 78712

² Now with ERM-Southwest, Austin, Texas

³ Now with the Department of Civil/Environmental Engineering, Carleton University, Ottawa, Ontario

Fate of Volatile Organic Compounds in Wastewater Collection Systems

Volume I: Summary of Research Components

RAC Project No. 577G

Submitted to the Ontario Ministry of Environment and Energy

by

Richard L. Corsi¹ (principal investigator)
School of Engineering, University of Guelph

Gordon Hayward (co-investigator)
School of Engineering, University of Guelph

John Bell (co-investigator)
Enviromega Ltd and School of Engineering, University of Guelph

Chris Quigley², Arlene Whitmore³, Michelle Swanston
School of Engineering, University of Guelph

1. Now with the Department of Civil Engineering, The University of Texas at Austin, Austin, Texas 78712
2. Now with ERM-Southwest, Austin, Texas
3. Now with the Department of Civil/Environmental Engineering, Carleton University, Ottawa, Ontario

October, 1994

Copyright: Queen's Printer for Ontario, 1994. This publication may be reproduced for non-commercial purposes with appropriate attribution.

Disclaimer

This report was prepared for the Ontario Ministry of Environment and Energy as part of a Ministry funded project. The views and ideas expressed in this report are those of the author and do not necessarily reflect the views and policies of the Ministry of Environment and Energy, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. The Ministry, however, encourages the distribution of information and strongly supports technology transfer and diffusion. Any person who wishes to republish part or all of this report should apply for permission to do so to the Research and Technology Section, Fiscal Planning and Information Management Branch, Ontario Ministry of Environment and Energy, 135 St. Clair Avenue West, 11th Floor, Toronto, Ontario, M4V 1P5, Canada.

TABLE OF CONTENTS

1. Introduction	
1.1 Problem Definition	1-1
1.2 Objectives of Research	1-4
1.3 Scope of Research	1-4
1.4 Organization of Report	1-6
2. Literature Review	
2.1 Approach	2-1
2.2 Summary by Subject	2-2
2.3 References by Section	2-10
3. VOC Emissions from Sewers in Metropolitan Toronto	
3.1 Background	3-1
3.2 Experimental Methodology	3-3
3.3 Results and Discussion	3-7
3.4 Additional Monitoring	3-12
3.5 Summary and Conclusions	3-12
3.6 References	3-13
4. Gas-Liquid Mass Transfer Along Sewer Reaches	
4.1 Background	4-1
4.2 Experimental Methodology	4-4
4.3 Results and Discussion	4-12
4.4 Summary and Conclusion	4-20
4.5 References	4-21
5. Biodegradation of VOCs in Sewers	
5.1 Background	5-1
5.2 Experimental Methodology	5-1
5.3 Results and Discussion	5-3
5.4 Summary and Conclusion	5-6
6. Additional Research	
6.1 Gas-Liquid Mass Transfer at Drop Structures	6-1
6.2 Formation of Chloroform	6-2
7. Integrated Fate Model	7-1
8. Conclusions and Recommendations	
8.1 Summary	8-1
8.2 Major Conclusions	8-1
8.3 Recommendations for Future Research	8-2

LIST OF TABLES

1.1	Target compounds for experiments and sampling events	1-8
3.1	Concentrations of target VOCs in the MCI (events 1-4)	3-16
3.2	Emissions rates for the MCI and four treatment plants in Ontario	3-16
3.3	Aqueous concentrations and stripping efficiencies (MCI events 5 and 6)	3-17
4.1	Physicochemical properties of tracers used in mass transfer experiments	4-24
4.2	Flow conditions and tracer concentrations for mass transfer experiments	4-24
4.3	Sewer operating conditions for mass transfer experiments	4-25
4.4	Experimental and predicted mass transfer coefficients	4-26
5.1	Suspended biomass concentrations in sewers	5-7
5.2	Parameters and results of biodegradation/volatilization modeling	5-8

LIST OF FIGURES

3.1	Simplified illustration of the Massey Creek Interceptor	3-17
3.2	Gas flowrates exiting manhole 3 (MCI, event 4)	3-18
3.3	Variations in TNMHC concentration in MCI headspace (event 4)	3-18
3.4	Target compounds emissions from the MCI (event 1)	3-19
3.5	Target compound emissions from the MCI (event 2)	3-19
3.6	Target compound emissions from the MCI (event 4)	3-20
3.7	TNMHC emissions from the MCI (event 4)	3-21
4.1	Experimental system to determine mass transfer coefficients (#1)	4-27
4.2	Experimental system to determine mass transfer coefficients (#2)	4-27
4.3	Relationship between potential energy dissipation and mass transfer coefficients	4-28
4.4	Predicted sewer half-lengths for 1,1,1-trichloroethane	4-28
5.1	Toluene concentration versus time for sterile control experiment	5-9
5.2	Perchloroethylene concentration versus time for sterile control experiment	5-9
5.3	Toluene concentration versus time (wastewater only)	5-10
5.4	Toluene concentration versus time (wastewater and tag)	
5.5	Toluene concentration with intermediate injection (wastewater and tag)	5-11
5.6	Toluene concentration with intermediate injection (wastewater, tag and yeast)	5-11
5.7	Perchloroethylene concentration versus time (wastewater, PERC and toluene only)	5-12
5.8	Perchloroethylene concentration versus time (wastewater, tag, PERC, and toluene)	5-12

ADDITIONAL VOLUMES

- Volume II. VOC Emissions from Sewers in Metropolitan Toronto
- Volume III. Gas-Liquid Mass Transfer Along Sewer Reaches
- Volume IV. Biodegradation of VOCs in Sewers
- Volume V. Gas-Liquid Mass Transfer at Drop Structures
- Volume VI. Formation of Chloroform: Pre-Discharge
- Volume VII. Formation of Chloroform: Post-Discharge
- Volume VIII. Model Documentation

ACKNOWLEDGEMENTS

The research described in this report could not have been completed without the commitment and financial resources provided by the Ontario Ministry of Environment and Energy. Additional funding was provided by Environment Canada and the Natural Sciences and Engineering Research Council (NSERC) of Canada.

The research steering committee (RSC) for this project consisted of Henryk Melcer, Victor Lim, and Peter Steer. During this project the RSC was headed by three separate liaison officers including (in reverse chronological order), Dr. Benjamin Campbell, Ron Seca, and the late Rob Paine. The research effort was facilitated by the understanding, technical advice and encouragement of the RSC. We would like to dedicate this report to Rob Paine, our first liaison officer. Rob was truly a gentle man and someone who we will remember as a tremendous liaison officer. Most importantly, he will be remembered as a friend.

Field sampling in Metropolitan Toronto could not have been completed without the cooperation of the Metropolitan Works Department of Toronto. We wish to thank Peter Vink for his assistance with coordinating each sampling event. Experiments related to gas-liquid mass transfer along sewer reaches could not have been completed without the cooperation of the City of Guelph's Department of Waterworks. We wish to thank Mr. John Sanvido for his cooperation and support, and Graham Granger and Scott Dickieson for their assistance in the field.

Field sampling events and biological experiments could not have been successfully completed without the willing, enthusiastic support of Dr. Hung Lee of the Department of Environmental Biology, and several students and staff members in the School of Engineering, at the University of Guelph. In particular, we wish to thank (in alphabetical order) Sandra Ausma, Melanie Dehaan, Graham Gagnon, Jeff Kemp, Perry Martos, Leonard Seed, Jennifer Shepherd, and Doug Thompson.

Finally, we wish to acknowledge the administrative staff of the School of Engineering at the University of Guelph for assisting with all of those "little things" that are often forgotten by university researchers. We are particularly grateful to Peggy Coghlan, Susan Lewis and Merie Hiskett. Thanks for the scheduling of appointments, summaries of accounts, purchase orders, and much more.

1. INTRODUCTION

1.1 PROBLEM DEFINITION

Volatile organic compounds (VOCs) are organic chemicals that have an affinity for the gas phase and that can easily volatilize from water to air upon contact with an air-water interface. They are used in a wide variety of applications ranging from household cleaners to fuel additives, and commercial and industrial solvents. They are subsequently discharged to municipal wastewater collection systems (WCS) from a large number of sources including commercial enterprises, industries, public institutions, and residential households.

There are many concerns regarding the presence of VOCs in wastewater, including:

1. Although most VOCs do not have a high affinity for adsorbing to solid particles and biomass, those that do can lead to sludge contamination with possible emissions or leaching from sludge handling, treatment and disposal facilities.
2. At high enough concentrations, some VOCs can cause upsets of biological reactors at wastewater treatment plants.
3. Although VOCs are often effectively removed from wastewater in secondary wastewater treatment plants (> 90% removal is common), at high influent concentrations the corresponding levels remaining in an effluent stream may be a concern in terms of toxicity effects on aquatic receiving systems.
4. Accumulation of VOCs in poorly ventilated sewer atmospheres can lead to explosion hazards.
5. Many VOCs are classified as toxic air contaminants (TAC) which at high enough gaseous concentrations can lead to acute occupational health risks to treatment plant employees, and potential chronic health risks to plant employees and the general public.

6. Many VOCs are classified as reactive organic gases (ROGs) which, if emitted from wastewater collection or treatment systems to the ambient atmosphere can contribute to the formation of tropospheric ozone, particularly in urban airsheds.

Necessity for the aforementioned concerns is not well documented, and the relative importance of each concern is speculative at best. In large part, these uncertainties are due to a general lack of understanding of the fate of VOCs in wastewater, particularly in wastewater collection systems. An improved understanding of the fate of VOCs in WCS is essential before the following questions can be adequately addressed:

1. Do mass loadings of VOCs in the influent streams of wastewater treatment plants represent a small or large fraction of total VOC mass discharges to WCS?
2. If mass discharges of VOCs to WCS are much greater than mass flows in treatment plant influent streams, can it be assumed that the difference is emitted to the atmosphere (i.e., are other removal mechanisms such as biodegradation important in sewers?).
3. If the major fraction of VOC removal from WCS is due to atmospheric emissions, how do the emissions distribute themselves throughout a WCS?
4. If VOC emissions from WCS occur at a small number of locations, do the emissions constitute a public health concern?
5. Do VOC emissions from WCS represent a significant ROG loading to urban air basins?
6. If VOC emissions from WCS are significant in terms of either TAC or ROG, what are the most appropriate methods for controlling such emissions?
7. Is it possible to develop a mathematical/computational model of the fate of VOCs in WCS that will allow A) predictions of the fate of existing and new VOC discharges, B) assessment of VOC control options, and C) a

tool for assisting in the development of sewer use by-laws for VOC discharges?

These questions are all important, and prior to this study could not be addressed adequately given the paucity of knowledge related to VOCs in WCS. During the course of this study, significant strides were made toward better understanding the fate of VOCs in municipal wastewater collection systems, and toward answering many of the previously unanswered questions posed above.

Because of the near complete lack of knowledge related to the fate of VOCs in WCS, it was necessary to begin understanding the subject through basic research regarding the fundamental physical, chemical, and biological mechanisms that affect the fate of VOCs in untreated wastewater. The basic processes which affect the fate of VOCs following their discharge to WCS include:

1. mass transfer between wastewater and overlying sewer atmospheres
2. formation of VOCs (i.e., formation of chloroform following hypochlorous acid discharges to WCS)
3. biodegradation of VOCs by microorganisms suspended in wastewater and attached to wetted sewer walls
4. adsorption/desorption of VOCs to/from solid particles
5. gas exchange (ventilation) between sewer and ambient atmospheres

This complex system of mechanisms is further complicated by several environmental factors, wastewater fluid and flow characteristics, and VOC physicochemical properties that affect each mechanism, and the fact that all mechanisms act simultaneously and thus influence each other. Clearly, one of the reasons that there is a lack of published literature on the fate of VOCs in WCS stems from the complex nature of the VOC/WCS system.

In 1990, the Ontario Ministry of Environment and Energy (MOEE) listed as one of its areas of research needs "Volatile Chemicals in Sewers and their Treatment" (issue WA03). In July, 1991, the MOEE awarded a three-year grant

to researchers at the University of Guelph to address the fundamental mechanisms which affect the fate of VOCs in wastewater collection systems. Combined with smaller amounts of NSERC and Environment Canada funding, funding from MOEE allowed the initiation of an intensive research program to study and improve the existing knowledge base related to each of the fate mechanisms listed above. This report and the additional volumes described below provide the findings of the aforementioned research.

1.2 OBJECTIVES OF RESEARCH

The overall objective of this study was to improve the existing base of scientific knowledge associated with the fate of VOCs in wastewater collection systems. Specific objectives included:

1. Assess the importance of competing fate mechanisms for VOCs.
2. Investigate gas-liquid mass transfer of VOCs along sewer reaches.
3. Quantify VOC emissions from a minimum of two municipal sewers in Toronto.
4. Develop a model to predict the fate of VOCs in wastewater collection systems.

1.3 SCOPE OF RESEARCH

Objectives 1 and 2 were completed through a series of laboratory and field experiments to investigate:

- formation of chlorinated VOCs following commercial bleach discharges to sewers (lab)
- biodegradation of VOCs by suspended and attached microorganisms in sewers (lab)
- gas-liquid mass transfer at sewer drop structures (pilot)
- gas-liquid mass transfer along sewer reaches (field)

Not all of these experiments could be completed within the scope of this research project. However, supplementary funding from NSERC and Environment Canada made it possible to complete each of the experiments described above. In particular, laboratory experiments to investigate chlorinated VOC formation were funded by an operating NSERC grant. Pilot studies of VOC mass transfer at drop structures were funded by a contract with Environment Canada's Wastewater Technology Centre. Initially, it was intended to use supplementary funding to study VOC adsorption to solid particles suspended in wastewater. These studies could not be completed given the resources which were available. Efforts to quantify natural air exchange between sewer and ambient atmospheres were also reduced to monitoring of sewer ventilation during field sampling events.

Sampling events were completed in three operating municipal sewers in metropolitan Toronto in order to quantify VOC emissions. This required a coupling of air exchange rates and headspace VOC concentrations. Two of the targeted sewer reaches were located in High Park, west of downtown Toronto. The third was located in Scarborough, east of downtown Toronto. Based on preliminary monitoring, the latter reach was observed to emit far greater quantities of VOCs and became the focus of this research effort.

Information collectively gained through all of the experiments described above were assimilated and used to develop a VOC fate model for WCS reaches (objective 4). The model was also evaluated based on data collected during the monitoring events described above.

Analysis of all volatile priority pollutants or volatile contaminants targeted by Ontario's Municipal Industrial Strategy for Abatement (MISA) was beyond the scope of this study. The research effort was therefore focused on a smaller list of target VOCs developed in consultation with the research steering committee (RSC). The target compounds are listed in Table 1.1. Methylene chloride was later removed from the list, again in consultation with the RSC, due to laboratory/analytical problems. During field sampling, a few additional VOCs, i.e., above and beyond those listed in Table 1.1, were identified and/or quantified.

1.4 ORGANIZATION OF REPORT

Research funded by the MOEE led to the production of three masters theses in Environmental Engineering at the University of Guelph, as well as several conference and journal publications. Supplementary funding from NSERC and Environment Canada led to one additional masters thesis and several conference papers.

This report (volume I) is intended to provide a brief summary of the various research components described above. Detailed literature reviews, descriptions of experimental methodologies, and discussions of experimental results are provided on additional volumes which correspond to student theses and conference proceedings.

A very brief review of relevant literature is provided as Chapter 2 of this report. Much more detailed reviews are provided in supplemental volumes.

Chapter 3 of this report provides a summary of important findings related to sampling at one of three municipal sewers tested during this project. Additional details regarding the sewer described in this volume as well as the other two sewers studied are provided in volume II.

Chapter 4 corresponds to field experiments involving volatile tracers to back-calculate mass transfer coefficients for two operating sewers in the City of Guelph. A summary of important findings is presented. Details of the research effort are provided as volume III.

Chapter 5 of this report provides a summary of research related to biodegradation of VOCs in sewers. Both suspended and attached-growth microbial populations are considered. Details of the research effort are provided in volume IV.

Chapter 6 is intended to summarize related research funded by NSERC and Environment Canada. The summary is very brief. However, significant details are presented as volumes V, VI, and VII.

Chapter 7 is intended to serve as a very brief summary of the model developed to predict VOC emissions from operating gravity-flow sewers. Technical information and user documentation are provided as volume VIII.

Finally, Chapter 8 is intended to provide a concise summary of the important conclusions stemming from the many components of this research effort. A set of recommendations for future study are also provided.

Table 1.1. Target compounds for experiments and sampling events

Benzene
Chlorobenzene
Chloroform
1,4-Dichlorobenzene
Dichloromethane (methylene chloride)
Ethylbenzene
Tetrachloroethene (perchloroethylene)
Toluene
1,1,1-Trichloroethane
Trichloroethene (TCE)
Xylenes (all isomers)

2. LITERATURE REVIEW

2.1 APPROACH

At the beginning of this study we completed an extensive literature review associated with volatile chemicals in water and wastewater, and have made significant progress in reviewing the subsequent literature. Following the initial review, we continued to review literature during the entire course of the three-year study. This chapter involves a brief summary of the papers that were found and reviewed at the beginning of the research effort. Comprehensive reviews of literature related to specific research topics are provided in volumes II through VII.

For the initial literature review, our approach was to investigate three primary sources of information:

- papers and reports that had been collected during previous research, i.e., that the research team already had on file
- follow-up reviews of references listed in the aforementioned compilation of papers and reports
- computer-assisted CHEM ABSTRACTS bibliographic data base

In total, we assembled and reviewed 166 technical papers and reports, all of which are documented at the end of this chapter. Surprisingly, the bibliographic search did not lead to identification of many papers beyond those which had already been obtained through the other two primary sources. Exceptions were in the general areas of biodegradation of VOCs in wastewater and formation of halogenated VOCs following chlorine discharges in water and wastewater.

Of the 166 papers/reports, only 13 were related to organic chemicals in sewers. Only two of those related directly to the issues that were addressed during this study, and one of those (Corsi, 1991) was published based on preliminary work completed for this project.

We have divided literature references into 14 categories as indicated in the references list at the end of this chapter. Brief reviews of each category are provided below.

2.2 SUMMARY BY SUBJECT

Levels and Occurrences of VOCs in Sewers

Levins *et al.* (1981) monitored USEPA priority pollutants in wastewaters flowing through WCS in four U.S. cities. Thirteen VOCs were detected in the four systems, and VOC concentrations in the aqueous phase generally increased from residential to commercial and industrial sewers. Average concentrations for individual VOCs were less than 10 µg/l and 25 µg/l in residential and commercial sewers, respectively. Concentrations in industrial sewers ranged from less than 1 µg/l to 100 µg/l for individual VOCs, with average concentrations exceeding 50 µg/l for ethylbenzene, tetrachloroethene, toluene, 1,1,1-trichloroethane, and trichloroethene. Monteith (1987) tabulated levels of several VOCs observed in the influent streams of several municipal wastewater treatment plants in Ontario. Although the data indicate variations in VOC concentrations entering wastewater treatment plants (i.e., exiting WCS), the study was not intended to provide concentrations within or losses from WCS.

Two research groups have reported levels of organic contaminants in sewer atmospheres. In Cincinnati, condensible saturated aliphatics were the predominant chemical group in non-residential sewers (Barsky *et al.*, 1986). Saturated halogenated aliphatics predominated during several sampling periods. Aromatics and halogenated alkenes were generally minor components of sewer atmospheres. Total organic concentrations were generally less than 100 ppm (benzene equivalents). Similar concentrations were observed in an operating main interceptor in Sacramento, California (Huang *et al.*, 1979). Wide concentration variations were observed on a daily basis. Modal hydrocarbon concentrations for each of four sampling events had a boiling point of approximately 160 °C, and compounds at that boiling point accounted for between 32 and 82% of total hydrocarbon concentrations in the interceptor atmosphere.

Assessment: At the beginning of this study, the existing literature was sparse on actual speciated VOC concentrations in sewer atmospheres and in wastewater flowing through various sections of WCS. It was not possible to extrapolate existing data to conditions in urban areas in Ontario. Thus, *the research completed during this project (Chapter 3 and Volume II) provides novel information and contributes significantly to existing knowledge related to the occurrence of VOCs in municipal sewers.*

VOCs in Sewers: Other

Kyosai *et al.* (1981) coupled laboratory experiments with mathematical predictions of dichloromethane losses from wastewater in WCS. However, their predictions were highly simplified, including an assumption of infinite ventilation (i.e., completely open sewer systems). Corsi (1989 and 1991) and Corsi *et al.* (1991) completed more rigorous mathematical modeling and field experiments and concluded that VOC emissions from sewers are highly sensitive to finite ventilation associated with enclosed WCS.

Fingas *et al.* (1988) studied methods of controlling fuel spills in sewers. Although their work did not focus on VOCs, their research approach of constructing a laboratory sewer simulator was innovative, and is being reviewed closely for possible use on this project.

Matthews (1975), Borne and Hobson (1980), and Toogood and Hobson (1980) both described the practical limits of VOC discharges to sewers. They emphasized many of the concerns described in Section 1 of this report, but did not offer specific information on VOC fate mechanisms or expected losses from sewers.

In a 1986 report to Congress, the USEPA (1986) suggested that little is known regarding the fate of VOCs in WCS, but that rapid desorption of VOCs should occur in well-ventilated systems. However, since that time most of the studies related to VOCs in wastewater have continued to focus on wastewater treatment systems.

Assessment: Although concerns regarding the discharge of VOCs to WCS have been raised in the literature, there have been no rigorous experimental or

field monitoring studies to quantify the fate, occurrence, or levels of VOCs in sewers. Limited modeling has suggested that relative removal of VOCs from sewers can be significant under some scenarios, and indicates the complex nature and coupling of fate mechanisms (i.e., ventilation and gas-liquid mass transfer).

Adsorption of VOCs to Solid Particles and Biomass

Three studies were identified with subsequent publications that describe adsorption and desorption of organic contaminants to solid particles and biomass in water and wastewater (Dobbs et al., 1989; Karickhoff et al., 1979; Tsezos and Bell, 1989).

Assessment: It may be possible to extend the results of the aforementioned studies to VOCs in WCS. However, none of the studies considered untreated wastewater. More importantly, they were all based on equilibrium conditions. The kinetics of VOC adsorption/desorption have not been effectively studied, and may be important given the time scales for wastewater transport and potentially small time scales for VOC volatilization in WCS. An assessment of adsorption kinetics was beyond the scope of this study.

Biodegradation of VOCs

Although 17 papers related to biodegradation of VOCs were identified, those that are associated with wastewater focus on biodegradation in aerobic and anaerobic reactors in municipal and industrial wastewater treatment plants. Nevertheless, these papers were reviewed as they indicated that some halogenated VOCs can be degraded under anaerobic conditions that might be similar to those observed in attached slime layers along wetted sewer walls. Furthermore, other papers provided information on experimental techniques that were useful for biological experiments completed during the third year of this study.

Assessment: Prior to this study, there was a paucity of published literature related to biodegradation of VOCs in WCS. Existing knowledge of VOC degradation in other environmental or engineered systems could not be

extrapolated to WCS with any degree of certainty. *The research completed during this project (Chapter 5 and Volume IV) sheds significant new insight on the importance of biodegradation as a VOC removal mechanism in sewers.*

Formation of Halogenated VOCs from Chlorine Discharges

In total, 31 papers associated with the formation of trihalomethanes following chlorine discharges to water and wastewater were identified and reviewed. However, only one of those (Aldridge *et al.*, 1976) dealt with chlorine injections into raw wastewater.

Assessment: A significant amount of work has been completed to quantify chloroform formation in water and wastewater. However, prior to this study little work had been completed to assess the formation of halogenated VOCs in untreated wastewater following commercial bleach discharges to WCS. Furthermore, factors affecting the formation of chloroform and other trihalomethanes in WCS (e.g., ammonia concentrations, pH, temperature) had not been reported. Based on previous studies, it was not possible to develop a fate model for sewers that incorporates chloroform formation, even from an empirical standpoint. There was also little information related to the formation of chloroform prior to discharge to municipal sewers, e.g., from residential washing machines. *The "additional" research completed using NSERC funds and reported in Chapter 6 and Volumes VI and VII is therefore novel and indicates the relative importance of chloroform formed in sewers versus chloroform formed prior to discharge to sewers.*

Gas-Liquid Mass Transfer: Reaches

In total, 22 papers/reports related to gas-liquid mass transfer along reaches and channels were identified and reviewed. These included some of the more commonly referenced works related to oxygen absorption to water. Several of these were omitted from the review process. However, it is worth studying oxygen transfer along reaches as the fundamental mechanisms that affect oxygen absorption also affect volatilization of many VOCs from water and wastewater.

Of the 22 references listed at the end of this chapter, only five dealt directly with WCS (Corsi *et al.*, 1989; Jensen and Hvitved-Jacobsen, 1990 and 1991; Parkhurst and Pomeroy, 1972; USEPA, 1974), and each of those focussed on oxygen transfer. However, Jensen and Hvitved-Jacobsen (1991) presented an interesting approach to studying gas-liquid mass transfer in operating WCS. Portions of their approach were adopted for the experiments completed in this study. All of the remaining papers dealt with oxygen absorption or VOC volatilization from natural waterways.

Assessment: Prior to this study, there had been only a limited amount of work related to gas-liquid mass transfer of volatile chemicals in operating WCS. There had not been enough work completed to develop a mechanistic model for mass transfer of VOCs, or to evaluate the potential for modifying existing oxygen absorption models to predict gas-liquid mass transfer of VOCs in WCS. *The experiments completed for this study (Chapter 4 and Volume III) provided the information required to develop and evaluate such a model.*

Gas-Liquid Mass Transfer: Hydraulic Structures

Nine papers related to gas-liquid mass transfer at hydraulic structures, particularly drops/waterfalls, were identified in the published literature. Of these, only one dealt with wastewater (Pincince, 1991), and it focused on oxygen transfer at clarifier weirs. Seven of the remaining eight papers focused entirely on oxygen transfer to clean water, and the remaining paper by Machlachlan *et al.* (1990) provided a conceptual model for VOC losses at waterfalls, in particular Niagara Falls.

Assessment: As stated above for reaches, oxygen can be theoretically related to VOC mass transfer. However, most of the existing literature related to hydraulic structures is highly empirical, and based on clean water studies. *The experimental results obtained during this study (Chapter 6 and Volume V) go well beyond those previously available to address VOC emissions from sewer drop structures.*

Gas-Liquid Mass Transfer: Other

An additional 17 references are related to gas-liquid mass transfer, but not to transfer along reaches or at drop structures, were identified and reviewed. Many of these corresponded to oxygen or VOC mass transfer during diffused bubble aeration or mechanical surface aeration in wastewater treatment plants (Kyosai and Rittmann, 1991; Melcer *et al.*, 1989; Mihelcic *et al.*, 1991; Roberts *et al.*, 1984). Some were even more general and described the fundamental mechanisms that affect mass transfer at gas-liquid interfaces (Danckwerts, 1951; Higbie, 1935; Lewis and Whitman, 1924; Mackay and Patterson, 1986; Mackay and Wolkoff, 1973; Matter-Muller *et al.*, 1981). Despite the fact that none of these papers/reports relates directly to WCS, there was some value in reviewing them as many of the fundamental mechanisms affecting gas-liquid mass transfer are analogous between WCS, wastewater treatment processes, and natural waterways. Furthermore, some of the papers/reports provided information that was of value for relating oxygen transfer to VOC transfer (Chao *et al.*, 1987; Daniil and Gulliver, 1988; Smith *et al.*, 1980), and suggested the relative importance of gas-phase mass transfer resistances for several VOCs and semi-VOCs in well-mixed water and wastewater systems (Munz and Roberts, 1989; O'Connor, 1983).

Assessment: General papers/reports that describe gas-liquid mass transfer in WCS were not identified in the published literature. *This underscores the importance of the many publications that have resulted from this research effort.*

Ventilation of Sewers

Seven papers/reports that describe ventilation of WCS were identified and reviewed. While some early work was completed to study forced ventilation of WCS (Pomeroy, 1945; Studley, 1939), there has been little work completed to quantify factors that cause natural ventilation of WCS. However, factors that are believed to most influence sewer ventilation include barometric pressure gradients, liquid drag, rise and fall of wastewater, eduction by wind, and differences in temperature between sewer and ambient atmospheres (Corsi *et al.*, 1989; Pescod and Price, 1981 and 1982).

Corsi *et al.* (1989) used theoretical fluid mechanical calculations coupled with extensions of work by Pescod and Price (1981 and 1982) to investigate the relative importance of several sewer ventilation mechanisms. Estimates of mean gas velocities caused by natural ventilation mechanisms were reported. An important conclusion was that an assumption of infinite ventilation can significantly overestimate VOC emissions under conditions of low ventilation and/or for VOCs with low Henry's law constants. However, such an assumption may be valid for VOCs with high Henry's law constants and/or conditions of high ventilation which might be found in combined sanitary/storm sewers or residential areas with many openings between sewer and ambient atmospheres.

Assessment: An understanding of gas dynamics (ventilation rates and patterns) in WCS is critical for appropriate evaluation of the fate of VOCs in WCS, particularly emissions to the ambient atmosphere. Recent research has allowed an identification of those factors that are believed to most influence natural ventilation of WCS. However, reasonable estimates of ventilation rates for specific types of sewers or sewer reaches was not possible at the beginning of this study. *As part of the field sampling effort completed for this study (Chapter 3 and Volume II), air exchange rates were quantified for a naturally well-ventilated sewer reach in Toronto. This is significant as the results are believed to yield close to an upper-bound for natural air exchange rates in municipal sewers.*

VOC Emissions from Wastewater: Reported Measurements

Eleven papers/reports that provide actual measurements of VOC emissions from wastewater were reviewed. However, each of those publications dealt only with wastewater treatment systems.

Assessment: Prior to this study, there were no published papers/reports that quantified measured VOC emissions from WCS. *The results provided herein are therefore considered to be the first of their kind (Chapter 3 and Volume II).*

VOC Emissions from Wastewater: Reported Estimates

Five papers/reports were identified that provide mathematical estimates of VOC emissions from wastewater. All of the published literature dealt only with wastewater treatment systems.

Assessment: See assessment for 2.10 above.

Fate of VOCs in Wastewater

Eight papers/reports that discussed the general fate of VOCs in wastewater were identified and reviewed. However, there are additional publications listed in several other Appendix A reference sections that describe general fate mechanisms. All of these papers focussed on wastewater treatment, as opposed to collection, systems.

Assessment: *Prior to this study, there have been no previous publications which describe the general fate of VOCs in WCS.*

VOC Fate Models

Eighteen papers/reports that describe the development and/or application of VOC fate models to wastewater were identified and reviewed. However, all of those corresponded only to wastewater treatment systems. An exception is listed in reference Section B (VOCS IN SEWERS: OTHER). It included a description of a simple one-dimensional two-phase reactor model to predict VOC emissions from sewer reaches (Corsi, 1989; Corsi, 1991; Corsi *et al.*, 1991). However, while the model was apparently unique, it was admittedly simple and was intended as a "screening" tool. It included gas-liquid mass transfer as the only VOC removal mechanism, and offered no guidance as to appropriate gas flow rates in sewer atmospheres.

Assessment: Prior to this study, there had been the initiation of only one VOC fate model for sewer reaches. However, the model required a significant amount of expansion and evaluation before it could be used as a reliable fate model. *A major objective of this research was to provide the information necessary to*

improve such a model. That objective was accomplished, and the revised fate model is described in Chapter 7 and Volume VIII.

Physicochemical Properties of VOCs

The importance of chemical properties with respect to the fate of VOCs in WCS was recognized at the beginning of this research effort. In terms of volatilization and subsequent emissions, Henry's law coefficient is an important VOC property. Five papers were identified and reviewed that actually quantify air-water Henry's law constants (equilibrium partitioning coefficients) for a wide range of VOCs, many of which are included in our target list (see Table 1). For some of the target VOCs, e.g., tetrachloroethene, there is a wide range of reported Henry's law coefficients (up to a factor of 2) at the same temperatures in clean water.

Assessment: Physicochemical properties (including Henry's law coefficient) of the target VOCs are readily available in the literature. However, there are some discrepancies in the literature regarding properties of some of the target compounds, and there is a paucity of information relating to extension of clean water results to raw wastewater. It was beyond the scope of this study to address uncertainties in VOC properties.

2.3 REFERENCES BY SECTION

Levels and Occurrences of VOCs in Sewers

Barsky, J.B., *et al.*, "Simultaneous Multi-Instrument Monitoring of Vapors in Sewer Headspace by Several Direct Reading Instruments," *Environmental Research*, 39, 307 (1986).

Huang, J.Y.C., *et al.*, "Evaluation of Activated Carbon Adsorption for Sewer Odor Control," *Journal of the Water Pollution Control Federation*, 51 (5): 1054 (1979).

Levins, P., *et al.*, "Sources of Toxic Pollutants found in Influent to Sewage Treatment Plants 6. Integrated Interpretation," EPA/440/4-81/007, U.S. Environmental Protection Agency, Washington, D.C. (1981).

Monteith, H.D., "Fluctuations of Trace Contaminants in Sewage Treatment Plants," H. Melcer (Ed.), Canadian Association of Water Pollution Research and Control, Monograph Series on Advances in Water Pollution Research and Technology (1987).

VOCs in Sewers: Other

Borne, B.J., and Hobson, J.A., "Predicting Safe Concentrations of Volatile Organic Substances in Discharges to Sewers," *Progress in Water Technology*, **12** (3), 77 (1980).

Corsi, R.L., "Volatile Organic Compound Emissions from Wastewater Collection Systems," Doctoral Dissertation, University of California, Davis (1989).

Corsi, R.L., "VOC Emissions from Sewers," *Annual Meeting of the Water Pollution Control Federation*, Toronto, Ontario (October, 1991).

Corsi, R.L., Chang, D.P.Y., and Schroeder, E.D., "Emissions of Volatile and Potentially Toxic Organic Compounds from Wastewater Treatment Plants and Collection Systems (Phase II) - Volume 2 - Wastewater Collection System Study," Report to the California Air Resources Board, Contract No. A7-32-085 (1991).

Fingas, M.F., Hughes, K.A., and Bobra, A.M., "Fuels in Sewers: Behaviour and Countermeasures," *Journal of Hazardous Materials*, **19**, 289 (1988).

Kyosai, S., Houthoofd, J.M., and Petrasek, A.C. , Jr., "Desorption of Volatile Priority Pollutants in Sewers," U.S. Environmental Protection Agency, Cincinnati (1981).

Matthews, P.J., "Limits for Volatile Organic Liquids in Sewers. Part 1," *Journal of Effluent Water Treatment*, **15** (11): 565 (1975).

Toogood, S.J., and Hobson, J.A., "The Determination of Safe Limits for the Discharge of Volatile Material to Sewers," Water Res. Cent. Stvenage Lab., Stevenage/Herts., Engl., TR 142 (1980).

United States Environmental Protection Agency, "Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works," EPA/530-SW-86-004, U.S. Environmental Protection Agency, Washington, D.C. (1986).

Adsorption of VOCs to Solid Particles and Biomass

Dobbs, R.A., Wang, L., and Govind, R., "Sorption of Toxic Organic Compounds on Wastewater Solids: Correlation with Fundamental Properties," *Environ. Sci. Technol.*, **23** (9): 1092 (1989).

Karickhoff, S.W., D.S. Brown, and T.A. Scott, "Sorption of Hydrophobic Pollutants on Natural Sediments," *Water Research*, **13**, 241 (1979).

Tsezos, M., and Bell, J.P., "Comparison of the Biosorption and Desorption of Hazardous Organic Pollutants by Live and Dead Biomass," *Water Research*, **23** (5): 561 (1989).

Biodegradation of VOCs

Aggarwal, P.K., and Hinchey R.E., "Monitoring In-Situ Biodegradation of Hydrocarbons by Using Stable Carbon Isotopes," *Environ. Sci. Technol.*, **25**, 1178 (1991).

Barrio-Lage, G., et al., "Sequential Dehalogenation of Chlorinated Ethenes," *Environmental Science and Technology*, **20** (1): 96 (1986).

Bell, et al., "Estimating Treatability Parameters for Predicting the Fate of VOCs in Wastewater Treatment Plants," *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver, British Columbia (1991).

Bhatnagar, L., et al., "Anaerobic Biotreatment of Toxic Chlorinated Hydrocarbons," Poster presented at the *64th Annual Conference of the Water Pollution Control Federation*, Toronto, Ontario (1991).

Bouwer, E.J., and McCarty, P.L., "Transformation of 1- and 2- Carbon Halogenated Aliphatic Organic Compounds Under Methanogenic Conditions," *Applied and Environmental Microbiology*, **45** (4): 1286 (1983).

Fitzsimons, R., Ek, M., and Eriksson, K.L., "Anaerobic Dechlorination/Degradation of Chlorinated Organic Organic Compounds of Different Molecular Masses in Bleach Plant Effluents," *Environ. Sci. Technol.*, **24**, 1744 (1990).

Holder, G.A., Van Oorschot, R., and Hauser, J., "Experimental and Theoretical Studies of Sulfide Generation in Sewerage Systems," *Wat. Sci. Tech.*, **21**, 757 (1989).

Kincannon, D.F., and Stover, E.L., "Determination of Activated Sludge Biokinetic Constants for Chemical and Plastic Industrial Wastewater," EPA-600/2-83-073A, U.S. Environmental Protection Agency (1983).

Kincannon, D.F., et al., "Removal Mechanisms for Toxic Priority Pollutants," *Journal of the Water Pollution Control Federation*, **55** (2): 157 (1983).

Lawson, C.T., and Siegrist, S.A., "Removal Mechanism for Selected Priority Pollutants in Activated Sludge Systems," *1981 National Conference on Environmental Engineering, Proceedings of the ASCE Environmental Engineering Division Specialty Conference*, F.M. Saunders (Ed.), 356 (1981).

Matos J.S., and de Sousa, E.R., "Dissolved Oxygen in Small Wastewater Collection Systems," *Wat. Sci. Tech.*, **23**, 1845 (1991).

Patterson, J.W., and Kodukala, P.S., "Biodegradation of Hazardous Organic Pollutants," *Chemical Engineering Progress*, **77** (4): 48 (1981).

Schroder, H. Fr., "Chlorinated Hydrocarbons in Biological Sewage Purification - Fate and Difficulties in Balancing," *Water Science Technology*, **19**, 429 (1987).

Strand, S.E., Bjelland, M.D., and, Stensel, H.D., "Kinetics of Chlorinated Hydrocarbon Degradation by Suspended Cultures of Methane-Oxidizing Bacteria," *Research Journal of the Water Pollution Control Federation*, **62** (2): 124 (1990).

Strand, S.E., Wodrich, J.V., and Stensel, H.D., "Biodegradation of Chlorinated Solvents in a Sparged, Methanotrophic Biofilm Reactor," *Research Journal of the Water Pollution Control Federation*, **63** (6): 859 (1991).

Tabak, et al., "Prediction of Biodegradation Kinetics Using a Nonlinear Group Contribution Method," *1989 International Chemical Congress of Pacific Basin Societies Symposium on Structure/Activity and Structure Property Relationships (SARS) in Environmental Chemistry and Toxicology*, Honolulu, Hawaii (1989).

Yoshimura, K., "Studies of the Composition and the Biodegradation of the Water-Insoluble Materials formed in the Domestic Sewer System," *Gesuido Kyokaishi*, **20** (225): 26 (1983). - (in Japanese)

Formation of Halogenated VOCs from Chlorine Discharges

Aizawa, T. and Magara, Y., "Behavior of Organochlorinated Compound Precursors in Biological Treatment Processes," *Kagawa*, **31** (3/4): 173 (1982).

Aldridge, M.H., et al., "Characterization of Nonvolatile Organic Material During Physical-Chemical Treatment of the District of Columbia Raw Wastewater," *Water Resources Research Center, Washington Technical Institute, Washington, D.C.* (1976).

Amy, G.L., et al., "Chlorine Utilization during Trihalomethane Formation in the Presence of Ammonia and Bromide," *Environmental Science and Technology*, **18** (10): 781 (1984).

Chambon, *et al.*, "Survey of Trihalomethane Levels in Rhone-Alps (France) Water Supplies. Estimates on the Formation of Chloroform in Wastewater Treatment Plants and Swimming Pools," *Water Research*, 17 (1): 65 (1983).

Chou, T., Wistrom, A., Chang, D.P.Y., *et al.*, "Study of Haloform Formation during Wastewater Chlorination," Report to the Bay Area Air Toxics Group (1990).

Chow, B.M., and Roberts, P.V., "Halogenated Byproduct Formation by ClO_2 and Cl_2 ," *Proceedings of the ASCE*, 107 (EE4): 609 (1981).

Cooper, W.J., *et al.*, "Formation of Organohalogen Compounds in Chlorinated Secondary Wastewater Effluent," Chapter 34 in *Water Chlorination: Environmental Impact Health Effects*, R.L. Jolley (Ed.), Lewis Publishers, Inc., Chelsea, Michigan (1983).

Crawford, R.J., and Stryker, M.N., "Factors that Affect the Generation of Chloroform in Bleaching," *TAPPI Journal*, 71 (11): 151 (1988).

Dore, M., *et al.*, "Reactivity of Halogens with Aqueous Micropollutants: A Mechanism for the Formation of Trihalomethanes," *Journal of the American Water Works Association*, 74 (2): 103 (1982).

Glaze, W.H., *et al.*, "Analysis of Chlorinated Organic Compounds Formed During Chlorination of Wastewater Products, EPA-600/4-82-072, U.S. Environmental Protection Agency (1982),

Glaze, W.H., *et al.*, "Analysis of Disinfection By-Products in Water and Wastewater," *International Journal of Environmental Analytical Chemistry*, 7 (2): 143 (1979).

Glaze, W.H., *et al.*, "Analysis of New Chlorinated Organic Compounds Formed by Chlorination of Municipal Wastewater," *Proceedings of the Conference on the Environmental Impact of Water Chlorination* (1975).

Helz, G.R., Uhler, A.D., and Sugam, R., "Dechlorination and Trihalomethane Yields," *Bulletin of Environmental Contamination and Toxicology*, 34 (4): 497 (1985).

Hemming, J., and Holmbom, B., "Formation of Potentially Hazardous By-Products on Chlorination of Humic Water and Kraft Pulp Mill Effluent," *Aqua Fennica*, 15 (2): 263 (1985).

Henderson, J.E., "GC/MS Analysis of Chlorinated Organic Compounds in Municipal Wastewater After Chlorination," Doctoral Dissertation, North Texas State University (1982).

Hocenski, V., Picer, M., and Picer, N., "Production of Lipophilic Volatile Organohalogen Materials During Laboratory Chlorination of Some Waste

Water and Polluted River Water Samples from Yugoslavia," *Wat. Res.*, **22**, 543 (1988).

Hunter, J.V., Busby, M.M., and Chang, H., "Influence of Industrial Wastes on the Formation of Volatile Halogenated Organics During Effluent Chlorination," *Proceedings of the 40th Industrial Waste Conference*, 631 (1985).

Hunter, J.V., Toffoli, G., and Muleller, R., "Origins of Volatile Halogenated Compounds in Chlorinated Effluents from Wastewater Treatment Plants Containing Different Industrial Waste Contributions," *Proceedings of the 41st Industrial Waste Conference*, 401 (1987).

Ishikawa, T., Ose, Y., and Sato, T., "Organohalides Formation by Chlorination of Wastewater," *Proceedings of the Colloquium on Aquatic Environment in Pacific Region*, Taipai, Taiwan, 245 (1978).

Itoh, S.I., Naito, S., and Unemoto, T., "Acetoacetic Acid as a Potential Trihalomethane Precursor in the Biodegradation Intermediates Produced by Sewage Bacteria," *Water Research*, **19** (10): 1305 (1985).

Kaczmar, S., et al., "Volatilization of Selected Haloforms from Aqueous Environments," *Environmental Toxicology and Chemistry*, **3** (1): 31 (1984).

Kananaugh, M.C., et al., "An Empirical Kinetic Model of Trihalomethane Formation: Applications to Meet the Proposed THM Standard," *Journal of the American Water Works Association*, 578 (1980).

Mori, B.T., Hall, K.J., and Blazeovich, J.N., "Effects of Chlorination of Some Volatile Organics in Primary Municipal Sewage Effluent," *Journal of Environmental Science and Health, Part A: Environmental Science and Engineering*, **A13** (7), 445 (1978).

Ram, N.M., Mussali, Y.G., and Chow, W., "Total Trihalomethane Formation During Targeted And Conventional Chlorination of Seawater for Biofouling Control," *Research Journal of the Water Pollution Control Federation*, **62** (6): 789 (1990).

Reiches, N.A., and Wilkins, J.R. III, "Multivariate Statistical Relationships Between Routine Water Plant Data and Trihalomethae Levels. Implications for Studies of Human Health," *Water Research*, **17** (12): 1881 (1983).

Richard, M.G., "Trihalomethane Formation from Humic Materials in Chlorinated Reclaimed Wastewater," Doctoral Dissertation, University of California, Berkeley (1980).

Rook, J.J., "Chlorination Reactions of Fulvic Acids in Natural Waters," *Environmental Science and Technology*, **11** (5): 478 (1977).

Sievers, R.E., et al., "Generation of Volatile Organic Compounds from Nonvolatile Precursors in Water by Treatment with Chlorine or Ozone," presented at *Water Chlorination: Environmental Impact and Health Effects*, 615, R.L. Jolley et al. (Eds.), Ann Arbor Sci., Ann Arbor, Michigan, 615 (1978).

Van Leeuwen, J., and Van Rossum, P.G., "Trihalomethane Formation during Sludge Bulking Control with Chlorine," *J. of the Inst. of Water. & Env. Mgmt.*, 4, 530 (1990).

Westrick, J.J., Cummins, M.D., and Cohen, J., "Breakpoint Chlorination/Activated Carbon Treatment: Effect of Volatile Halogenated Organics," EPA/600/2-78/165 (1978).

Yamamoto, K., Fukushima, M., and Oda, K., "Effects of Stirring on Residual Chlorine During Chlorination of Seawater Containing Ammonia Nitrogen," *Wat. Res.*, 24, 649 (1990).

Gas-Liquid Mass Transfer: Reaches

Churchill, M.A., Elmore, H.L., and Buckingham, R.P., "The Prediction of Stream Reaeration Rates," *Journal of the Sanitary Engineering Division, ASCE*, 88 (SA4), 1 (1962).

Corsi, R.L., Chang, D.P.Y., and Schroeder, E.D., "Prediction of Cross-Media VOC Mass Transfer Rates in Sewers based upon Oxygen Reaeration Rates," *Proceedings of the 82nd Annual Meeting of the Air and Waste Management Association*, Anaheim (1989).

Dobbins, W.E., "The Nature of the Oxygen Transfer Coefficient in Aeration Systems," Chapter 2-1 in *Biological Treatment of Sewage and Industrial Waste*, Volume 1, J. McCabe and W.W. Eckenfelder, Jr. (Eds.), Reinhold Publishing Company, New York, New York (1956).

Dobbins, W.E., "Mechanism of Gas Absorption by Turbulent Liquids," in *Advances in Water Pollution Research*, Volume 2., 61, W.W. Eckenfelder (Ed.), Pergamon Press, Ltd., New York, New York, (1964).

Gulliver, J.S., and Halverson, M.J., "Air-Water Gas Transfer in Open Channels," *Water Resources Research*, 25, 1783 (1989).

Frexes, P., Jirka, G.H., and Brutsaert, W., "Examination of Recent Field Data on Stream Reaeration", *Journal of Environmental Engineering, ASCE*, 110, 1179 (1984).

Isaacs, W.P., and Gaudy, A.F., "Atmospheric Oxygenation in a Simulated Stream," *Journal of the Sanitary Engineering Division, ASCE*, 94 (SA2), 319 (1968).

Jensen, N.A., and Hvitved-Jacobsen, T., "Tracer Measurements of Reaeration in Gravity Sewers," *Wat. Sci. Tech.*, 22, 279 (1990).

Jensen, N.A., and Hvitved-Jacobsen, T., "Method for Measurement of Reaeration in Gravity Sewers using Radiotracers," *Research Journal of the Water Pollut. Control Fed.*, **63**, 114 (1991).

Krenkel, P.A., and Orlob, G.T., "Turbulent Diffusion and the Reaeration Coefficient," *Transactions, ASCE*, **128** (paper 3491), 293 (1963).

Lau, Y.L., "Prediction Equation for Reaeration in Open-Channel Flow," *Journal of the Sanitary Engineering Division, ASCE*, **98** (SA6): 1063 (1972).

O'Connor, D.J., and Dobbins, W.E., "Mechanisms of Reaeration in Natural Streams," *Transactions, ASCE*, **123** (2934): 641 (1958).

Owens, M., Edwards, R.W., and Gibbs, J.W., "Some Reaeration Studies in Streams," *International Journal of Air and Water Pollution*, **8** (819): 469 (1964).

Parkhurst, J.D., and Pomeroy, R.D., "Oxygen Absorption in Streams," *Journal of the Sanitary Engineering Division, ASCE*, **98** (SA1): 101 (1972).

Rathbun, R.E., "Prediction of Stream Volatilization Coefficients," *Journal of Environmental Engineering, ASCE*, **116** (3): 615 (1990).

Rathbun, R.E., "Gas-Film Coefficients for Streams," *Journal of Environmental Engineering, ASCE*, **109** (5): 1111 (1983).

Rathbun, R.E., "Reaeration Coefficients of Streams - State-of-the-Art," *Journal of the Hydraulics Division, ASCE*, **103**, HY4, 409 (1977).

Rathbun, R.E., *et al.*, "Laboratory Studies of Gas Tracers for Reaeration," *Journal of Environmental Engineering, ASCE*, **104** (EE2): 215 (1978).

Tsivoglou, E.C., *et al.*, "Tracer Measurements of Atmospheric Reaeration - I. Laboratory Studies," *J. Water Pollut. Control Fed.*, **37**, 1343 (1965).

Tsivoglou, E.C., and Neal, L.A., "Tracer Measurements of Reaeration: II. Predicting the Reaeration Capacity of Inland Streams," *J. Water Pollut. Control Fed.*, **48**, 2669 (1976).

U.S. Environmental Protection Agency, "Process Design Manual for Sulfide Control in Sanitary Sewerage Systems," EPA 625/1-74-005, Office of Technology Transfer, Washington, D.C. (1974).

Wilson, G.T., and Macleod, N., "A Critical Appraisal of Empirical Equations and Models for the Prediction of the Coefficient of Reaeration of Deoxygenated Water," *Water Research*, **8** (6): 341 (1974).

Gas-Liquid Mass Transfer: Hydraulic Structures

Apted, R.W., and Novak, P., "Some Studies of Oxygen Uptake at Weirs," *Proceedings of the XV Congress, International Association for Hydraulic Research*, Paper B23, 177 (1973).

Avery, S.T. and Novak, P., "Modelling of Oxygen Transfer from Air Entrained by Solid Jets Entering a Free Water Recipient," *Proceedings of the XVII Congress, International Association for Hydraulics Research*, Paper A59, 1977, 467 (1977).

Avery, S.T., and Novak, P., "Oxygen Transfer at Hydraulic Structures," *Journal of the Hydraulics Division, ASCE*, **104**, 1521 (1978).

Gameson, A.L.H., "Weirs and the Reaeration of Rivers," *Journal of the Institute of Water Engineers*, **11**, 477 (1957).

Gameson, A.L.H., Vandyke, K.G., and Ogden, C.G., "The Effect of Temperature on Aeration at Weirs," *Water Engineering*, **62**, 489 (1958).

Holler, A.G., "The Mechanism Describing Oxygen Transfer from the Atmosphere to Discharge Through Hydraulic Structures," *Proceedings, XIV Congress, International Association for Hydraulics Research*, Paper A45, 373 (1971).

McLachlan, M., Mackay, D., and Jones, P.H., "A Conceptual Model of Organic Chemical Volatilization at Waterfalls," *Environ. Sci. Technol.*, **24**, 252 (1990).

Nakasone, H., "Study of Aeration at Weirs and Cascades," *Journal of Environmental Engineering, ASCE*, **113**, 64 (1986).

Pincince, A.B., "Transfer of Oxygen and Emissions of Volatile Organic Compounds at Clarifier Weirs," *Research Journal of the Water Pollut. Control Fed.*, **63**, 114 (1991).

Gas-Liquid Mass Transfer: Other

Chao, A.C., et al., "Influence of Temperature on Oxygen Transfer," *Journal of Environmental Engineering, ASCE*, **113** (4): 722 (1987).

Cohen, Y., Cocchio, W., and Mackay, D., "Laboratory Study of Liquid-Phase Controlled Volatilization Rates in the Presence of Wind Waves," *Environ. Sci. Technol.*, **12** (5): 553 (1978).

Danckwerts, P.V., "Significance of Liquid Film Coefficients in Gas Absorption," *Industrial and Engineering Chemistry*, **43** (6): 1460 (1951).

Daniil, E.I., and Gulliver, J.S., "Temperature Dependence of Liquid Film Coefficient for Gas Transfer," *Journal of Environmental Engineering, ASCE*, **114**, 1224 (1988).

Dilling, W.L., Tefertiller, N.B., and Kallos, G.J., "Evaporation Rates and Reactivities of Methylene Chloride, Chloroform, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Compounds in Dilute Aqueous Solutions," *Environmental Science and Technology*, **9** (9): 833 (1975).

Higbie, R., "The Rate of Exposure of a Pure Gas into a Still Liquid During Short Periods of Exposure." *Transactions, Amer. Inst. of Chem. Engrs.*, **31**. (1935).

Kyosai, S., and Rittmann, B.E., "Effect of Water-Surface Desorption on Volatile Compound Removal Under Bubble Aeration," *Research Journal of the Water Pollution Control Federation*, **63** (6): 887 (1991).

Lewis, W.K., and Whitman, W.G., "Principles of Gas Absorption," *Industrial and Engineering Chemistry*, **16**, 1215 (1924).

Mackay, D., and Paterson, S., "Model Describing the Rates of Transfer Processes of Organic Chemicals Between Atmosphere and Water," *Environmental Science and Technology*, **20** (8): 810 (1986).

Mackay, D., and Wolkoff, A.W., "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere," *Environmental Science and Technology*, **7** (7): 611 (1973).

Matter-Muller, C., *et al.*, "Transfer of Volatile Substances from Water to the Atmosphere," *Water Research*, **15**, 1271 (1981).

Melcer, H., *et al.*, "Stripping of Volatile Organic Compounds at Municipal Wastewater Treatment Plants," *Proceedings of the AWM/EPA International Symposium on Hazardous Waste Treatment: Biosystems for Pollution Control*, Cincinnati (1989).

Mihelcic, J.R., *et al.*, "Models for Stripping-Volatilization of VOCs from Wastewater", *Proceedings of the 84th Annual Meeting of AWMA*, Vancouver, British Columbia, Paper No. 91-92.7 (1991).

Munz, C. and Roberts, P.V., "Gas and Liquid-Phase Mass Transfer Resistances of Organic Compounds During Mechanical Surface Aeration," *Wat. Res.*, **23**, 589 (1989).

O'Connor, D.J., "Wind Effects on Gas-Liquid Transfer Coefficients," *Journal of Environmental Engineering*, ASCE, **109** (3): 731 (1983).

Roberts, P.V., *et al.*, "Volatilization of Organic Pollutants in Wastewater Treatment - Model Studies," EPA-600/2-84-047, U.S. Environmental Protection Agency, Cincinnati (1984).

Smith, J.H., *et al.*, "Prediction of the Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies," *Environ. Sci. Technol.*, **14**, 1332 (1980).

Ventilation of Sewers

Corsi, R.L., Chang, D.P.Y., and Schroeder, E.D., "Assessment of the Effects of Ventilation Rates on VOC Emissions from Sewers," *Proceedings of the WPCF/EPA Workshop on Air Toxics and POTWs*, Alexandria (1989).

Nishida, K., and Osako, M., "Determination of Hydrogen Sulfide in Wastewater and Sludge in Sewer Manholes and Required Amount of Ventilation," *Nippon Eiseigaku Zasshi*, **44** (2): 639 (1989). - (in Japanese)

Pescod, M.B., and Price, A.C., "Fundamentals of Sewer Ventilation as Applied to the Tyneside Sewerage Scheme," *Water Pollution Control*, **17** (1981).

Pescod, M.B., and Price, A.C., "Major Factors in Sewer Ventilation," *J. Water Pollut. Control Fed.*, **54**, 385 (1982).

Pomeroy, R., "The Pros and Cons of Sewer Ventilation," *Sewage Works Journal*, **17** (2): 203 (1945).

Studley, E.G., "Experimental Ventilation of the North Outfall Sewer of the City of Los Angeles," *Sewage Works Journal*, **11** (2): 264 (1939).

Thistlethwayte, D.K.B. (Ed.), "The Control of Sulphides in Sewerage Systems," Ann Arbor Science Publishers, Michigan (1972).

VOC Emissions from Wastewater: Reported Measurements

Allen, C.C., *et al.*, "Preliminary Assessment of Air Emissions from Aerated Waste Treatment Systems at Hazardous Waste Treatment Storage and Disposal Facilities," United States Environmental Protection Agency, Contract No. 68-02-3992 (1986).

Balogh, S.J., and Tiffin, P.L., "The Emission of Volatile Organic Compounds from Aerated Grit Chambers at the Metropolitan Wastewater Treatment Plant," *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver, British Columbia (1991).

Caballero, R.C., and Griffith, P., "VOC Emissions from POTWs," *Proceedings of the WPCF/EPA Workshop on Air Toxics and POTWs*, Alexandria (1989).

Chang, D.P.Y., "Emissions of Volatile and Potentially Toxic Organic Compounds from Wastewater Treatment Plants and Collection Systems (Phase II) - Volume 3 - Wastewater Treatment Plant Emissions - Experimental Phase," Report to the California Air Resources Board, Contract No. A732-085 (1992).

Chang, D.P.Y., "Emissions of Volatile and Potentially Toxic Organic Compounds from Wastewater Treatment Plants and Collection Systems (Phase II) - Volume 1 - Project Summaries," Report to the California Air Resources Board, Contract No. A732-085 (1992).

Lurker, P.A., *et al.*, "Aerial Organic Chemical Release from Activated Sludge," *Water Research*, **18** (4): 489 (1984).

Lurker, P.A., *et al.*, "Atmospheric Release of Chlorinated Organic Compounds from the Activated Sludge Process," *Journal of the Water Pollution Control Federation*, **54** (12): 1566 (1982).

Partridge, G.P., and Vuong, D.C., "Volatile Organic Carbon (VOC) Emissions from Biological Treatment Processes of Gasoline Tank Bottoms," *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver, British Columbia (1991).

Petrasek, A.C., Austern, B.M. and Neiheisel, T.W., "Removal and Partitioning of Volatile Organic Priority Pollutants in Wastewater Treatment," *Proceedings of the 9th U.S.-Japan Conference on Sewage Treatment Technology*, Tokyo (1983).

Ruby, M.G., Prokop, W.H., and Kalman, D.A., "Measurment of Odor Emissions from a Sewage Treatment Plant," *Proceedings of the 80th Annual Meeting of the Air Pollution Control Association*, New York, New York (1987).

Wood, K.N., Jann, P.R., and Whitecraft, W.K., "Volatile Organic Emissions from an Industrial Wastewater Treatment Facility," *Proceedings of the 83rd Annual Meeting of the Air and Waste Management Association*, Pittsburgh, Pennsylvania (1990).

VOC Emissions from Wastewater: Reported Estimates

Chang, D.P.Y., Schroeder, E.D., and Corsi, R.L., "Emissions of Volatile and Potentially Toxic Organic Compounds from Sewage Treatment Plants and Collection Systems," Report to the California Air Resources Board, Contract No. A5-127-32 (1987).

Corsi, R.L., Chang, D.P.Y., Schroeder, E.D., and Qiu, Q., "Emissions of Volatile and Potentially Toxic Organic Compounds from Municipal Wastewater Treatment Plants," *Proceedings of the 80th Annual Meeting of the Air Pollution Control Association*, New York, New York, 87-95.7 (1987).

Corsi, R.L., and Griffes, D.A., "VOC Emission Estimation Methods Applied to POTWs in the San Francisco Bay Area," Paper presented at the *American Institute of Chemical Engineers 1990 Summer National Meeting*, San Diego, CA (1990).

Noll, K.E., and DePaul, F.T., "Emissions of Volatile Organic Compounds from the Sewage Treatment Facilities of the Metropolitan Sanitary District of Greater Chicago - Volume I," Report to the Metropolitan Water Reclamation District of Greater Chicago (1987).

Silverman, G., "Air Emissions Associated with Publicly Owned Treatment Works in Santa Clara Valley," Memorandum from the Association of Bay Area Governments to the U.S. Environmental Protection Agency, Integrated Environmental Management Project (1985).

Fate of VOCs in Wastewater

Corsi, R.L., and Card, T.R., "VOCs in Wastewater: State of Understanding," *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver, British Columbia, 91-92.12 (June, 1991).

Freeman, R.A., "Air Stripping of Acrylonitrile from Wastewater Treatment Systems," *Environmental Progress*, 3 (1): 26 (1984).

Hannah, S.A., et al., "Comparative Removal of Toxic Pollutants by Six Wastewater Treatment Processes," *Journal of the Water Pollution Control Federation*, 58 (1): 27 (1986).

Meuser, J.W., and Cooke, W.M., "Fate of Semivolatile Priority Pollutants in a Wastewater Treatment Plant," EPA-600/2-81-056, U.S. Environmental Protection Agency (1981).

Strier, M.P., and Gallup, J.D., "Removal Pathways and Fate of Organic Priority Pollutants in Treatment Systems: Chemical Considerations," *Proceedings of the Industrial Waste Conference*, 37 (1983).

Sun, P.T., and Compennolle, R.V., "Behavior of Volatile Organics and Other Compounds in Refinery Activated Sludge Systems - A Review," presented at the *California Water Pollution Control Association Industrial and Hazardous Waste Conference* (1990).

United States Environmental Protection Agency, "Fate of Priority Pollutants in Publicly Owned Treatment Works - Vol 1.," EPA 440/1-82/303, U.S. Environmental Protection Agency, Washington, D.C. (1982).

Weber, W.J., and B.E. Jones, "Toxic Substance Removal in Activated Sludge and PAC Treatment Systems," *1984 Annual Conference of the Water Pollution Control Federation*, New Orleans (1984).

VOC Fate Models

Baillod, C.R., *et al.*, "Critical Evaluation of the State of Technologies for Predicting the Transport and Fate of Toxic Compounds in Wastewater Facilities," Report to the WPCF Research Foundation (1990).

Barton, D.A., "Intermedia Transport of Organic Compounds in Biological Wastewater Treatment Processes," *Environmental Progress*, 6 (4): 246 (1987).

Berglund, R.L., and Whipple, G.M., "Predictive Modeling of Organic Emissions," *Chemical Engineering Progress*, 46 (1987).

Blackburn, J.W., "Prediction of Organic Chemical Fates in Biological Treatment Systems," *Environmental Progress*, 6 (4): 217 (1987).

Card, T.R., and Corsi, R.L., "A Flexible Fate Model for VOCs in Wastewater," 1991 Annual Meeting of the Water Pollution Control Federation, Toronto, Ontario (1991).

Card, T.R., Corsi, R.L., and Witherspoon, J., "Toxic Air Contaminant Emissions from Wastewater: Estimation Methods," *Proceedings of the Air and Waste Management Association Conference on Air Toxics Issues in the 1990s: Policies, Strategies and Compliance*, King of Prussia, Pennsylvania (1991).

Corsi, R.L. and Card, T.R., "A Multi-Process General Fate Model for VOCs in Wastewater," *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver (1991).

Corsi, R.L., and Card, T.R., "Estimation of Air Toxics Emissions Using the Bay Area Sewage Toxics Emissions (BASTE) Model," 1991 Summer National Meeting of the AIChE, Pittsburgh, Pennsylvania (1991).

Corsi, R.L., and Card, T.R., "Estimation of VOC Emissions Using the BASTE Model," *Environmental Progress*, 10 (4): 290 (1991).

Corsi, R.L., Chang, D.P.Y., Schroeder, E.D., and Qiu, Q., "Modeling the Emissions of Volatile and Potentially Toxic Organic Compounds from Municipal Wastewater Treatment Plants," *Proceedings of the 80th Annual Meeting of the Air Pollution Control Association*, New York, New York, 87-95A.5 (1987).

Corsi, R.L., Schroeder, E.D., and Chang, D.P.Y., discussion of "Estimating Volatile Organic Compound Emissions from Publicly Owned Treatment Works," by E. Namkung and B.E. Rittmann, *J. Water Pollut. Control Fed.*, 61 (1), 95-96 (1989).

Corsi, R.L., *et al.*, "Modeling the Emissions of Volatile and Potentially Toxic Organic Compounds from Municipal Wastewater Treatment Plants,"



3. VOC EMISSIONS FROM SEWERS IN METROPOLITAN TORONTO

3.1 BACKGROUND

During the past three years, several studies have focused on the fate and control of VOCs in wastewater treatment systems (Bell *et al.*, 1988; Mihelcic *et al.*, 1993; Namkung and Rittmann, 1987). Much less attention has been given to determining the fate of VOCs in wastewater collection systems, and to quantifying VOC mass emissions from distributed openings in such systems. There is currently a paucity of information related to VOC discharges to, occurrences in, and losses from sewers. Thus, it is not possible to determine whether influent mass loadings to wastewater treatment facilities constitute a minor or major fraction of VOCs discharged to collection systems. Furthermore, in most municipal sewer networks and many on-site industrial sewers, the number of locations for gas exchange between sewer and ambient atmospheres makes field monitoring of emissions difficult on a large scale.

The USEPA (1986) completed a *Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works*. That report provided a summary of knowledge related to discharges and fate of hazardous compounds, including VOCs, in municipal wastewater. It also highlighted a general lack of knowledge regarding the fate of VOCs in wastewater collection systems. Similarly, Chang *et al.* (1987) investigated the potential for emissions of 16 VOCs at POTWs throughout California and reported that the lack of information related to VOCs in sewers makes it impossible to accurately quantify emissions from such systems.

A few researchers have reported levels of organic contaminants in sewer atmospheres. In Cincinnati, total organic compound concentrations were generally less than 100 parts per million by volume (ppm) in benzene equivalents (Barsky *et al.*, 1986). Similar concentrations were observed in an operating main interceptor in Sacramento, California (Huang *et al.*, 1979). Reid and McEvoy (1987) monitored sewer atmospheres in London, England. In a sewer receiving relatively small quantities of industrial discharge, benzene,

toluene, and trichloroethene concentrations in the sewer headspace were observed to be < 0.5, 5, and < 0.5 ppm, respectively. In a sewer reported to contain significant industrial discharges, benzene, toluene, and trichloroethene concentrations in the headspace were observed to be 52, 170, and 116 ppm, respectively. Levels of 1,4-dichlorobenzene and 1,2-dichlorobenzene were also observed to be 4 and 14 ppm, respectively. Thus, the range of total and speciated VOC concentrations in sewer atmospheres is large, and gaseous concentrations of individual VOCs in some municipal sewers can reach hundreds of parts per million by volume.

High gas concentrations of VOCs in sewers may not equate to high emissions, since VOC accumulation may occur without significant gas exchange between sewer and ambient atmospheres. Pescod and Price (1982) estimated air turnover rates of between 0.5 and 2.3 per day based on field experiments and modeling of oxygen mass balances in 0.45 to 3.0 m diameter sewers. Unfortunately, natural ventilation of sewers is not well understood and does not currently allow routine coupling of estimated ventilation rates with gas-phase concentrations to estimate VOC emissions.

In addition to ventilation, emissions of VOCs from sewers depend on the degree of mass transfer from wastewater to an overlying sewer headspace. Several recent papers have provided insight regarding gas-liquid mass transfer mechanisms and mass transfer coefficients in sewers (Corsi *et al.*, 1992; Corsi and Whitmore, 1992; Corsi *et al.*, 1993; Jensen and Hvitved-Jacobsen, 1991; Whitmore and Corsi, 1994;). These have included pilot and field experiments, as well as computational modeling, and suggest that, when present, large sewer drop structures dominate VOC stripping from wastewater.

Thus, conditions which are conducive to high VOC emissions from sewers include 1) significant VOC discharges in the aqueous phase, 2) the presence of drop structures which enhance gas-liquid mass transfer, and 3) high rates of headspace ventilation. A large municipal sewer interceptor which meets all three of these conditions was identified in Toronto, Ontario. Subsequent monitoring events were completed to determine concentrations of several target VOCs in the sewer headspace, headspace ventilation rates, VOC emission rates, and the relative importance of drop structures with respect to VOC stripping efficiency.

3.2 EXPERIMENTAL METHODOLOGY

Sampling Location

The field site selected for study was a large sewer interceptor (Massey Creek Interceptor: MCI) located in metropolitan Toronto, Ontario. Previous monitoring of MCI headspace gas indicated high concentrations of toluene, ethylbenzene, and xylenes, with identifiable concentrations of benzene and tetrachloroethene.

A schematic of the MCI is presented in Figure 3.1. Physical characteristics of the reach included a total length of 1.6 km, channel slopes ranging from 0.25 to 1.0%, pipe diameters ranging from 0.9 m to 1.2 m, 17 manholes (14 with highly perforated covers), and four drops ranging from 0.15 to 3.0 m in height. Distances, channel slopes and pipe diameters between any two manholes are listed in Figure 3.1. Flowing at half-full in the 0.25% channel slope section, the MCI conveyed wastewater at a rate of approximately 0.4 m³/s. For this study, typical mid-day flows were approximately 0.2 m³/s, with depths of 20 to 25 cm.

A preliminary reach inspection was performed prior to sampling to determine exact locations for emissions monitoring. This indicated that the downstream section of the interceptor bounded by manholes 7 and 31 contained the manholes through which the majority of natural outgassing occurred. This is depicted in Figure 3.1 by vertical arrows. In this section there were five highly perforated outgassing manhole covers, each containing 66 pickholes. Of the two-pickhole manhole covers, only one appeared to have outgassing. This manhole, MH31, was located at a junction box which connected a smaller sewer reach with the MCI. Elevation drops of greater than one meter were located at manholes 7, 8 and 10.

To ascertain the relative importance of emissions between the two and 66 pickhole manhole covers, ventilation rate and headspace samples were measured/collected at manhole 31 and manhole 1. Emissions from the highly perforated manhole cover exceeded those from the two pickhole manhole cover by between one and two orders of magnitude. Based on this finding, it

was decided to limit emissions monitoring to only highly perforated manhole covers.

Sampling Events

Six sampling events were completed. Four events involved measurement of gaseous emissions from the MCI. The fifth and sixth events consisted of liquid and gas sampling to determine the relative importance of VOC stripping across two drop structures (located at manholes 6 and 9) and along a reach characterized by near uniform flow conditions (located between manholes 3 and 6).

Three of the four gaseous emissions events were performed over approximately seven hour intervals; two on weekdays (Events 1 and 2) and the third on a Sunday (Event 3). The fourth gaseous emissions monitoring event (Event 4) covered a 24-hour period commencing at 6:00 hours on a weekday.

For the first three events headspace gas sampling and outgas flowrates were obtained from the following four manholes: MH7, MH6, MH5 and MH3. For Event 1 headspace samples were collected at 9:00, 1:00 and 16:00 hours. Event 1 outgas flowrates were measured at 9:00, 11:00, 13:00, 15:00 and 16:00 hours. Headspace samples were collected during Event 2 at 8:00, 10:30 and 15:30 hours. Outgas flowrates for Event 2 were measured at 8:00, 9:15, 10:30, 11:45, 13:30, 14:15 and 15:30 hours. Headspace sample collection and outgas flowrate measurements during Event 3 were performed at 9:00, 13:00 and 16:00 hours. During each sampling period, samples were first collected/measured at the furthest upstream manhole (MH7). The remaining manholes were then sequentially sampled in the direction of wastewater flow.

During event 4, headspace gas samples were collected at MH3. Headspace sampling was performed every two hours for a 24-hour period beginning at 6:00 hours. Outgas flowrates from MH3 were measured at 6:00, 8:00 and then hourly until 20:00 hours, followed by measurements at 22:00, 0:00, 2:00, 4:00 and 6:00 hours.

Total nonmethane hydrocarbon (TNMHC) measurements were also performed at MH3 at these times. In addition, TNMHC and outgas flowrates

were measured at MH7, MH6 and MH5 at 6:00, 8:00 and then hourly until 16:00 hours.

Wastewater sample collection was performed on two separate weekdays (Events 5 and 6) between 14:00 and 16:00 hours to determine VOC stripping efficiencies between MH9 and MH6, i.e. across two large drop structures. During Event 5, wastewater grab samples were collected at three locations along the MCI: MH9, MH6 and MH3. Starting at 14:00 hours a total of 11 samples, one taken approximately every ten minutes, were collected at MH9. A total of 11 wastewater samples at MH6 were similarly collected over 105 minutes. Eight wastewater samples were collected at MH3 spanning 105 minutes. During Event 6, wastewater samples were collected only at MH9 and MH6. The number of samples collected at each manhole were the same as for Event 5. During each event, 2-3 gas samples were collected in the MCI headspace at MH6 in accordance with the methods described below.

Sampling Methods

Estimation of speciated VOC emissions from the MCI during Events 1 through 4 required the acquisition and analysis of headspace gas samples and the measurement of outgas flowrates. Determination of TNMHC emissions during Event 4 necessitated additional TNMHC concentration measurements. Associated sample methodologies are described below.

A hot-wire anemometer was used to obtain sewer gas effluent velocities. Measurements were recorded with the anemometer probe flush with the manhole cover. At each manhole, velocity measurements were recorded over a traverse diameter including between three and seven pickholes. Measurements were repeated four times for each pickhole. A traverse average velocity was then calculated and used in conjunction with the measured total area of all pickholes to obtain a flowrate per manhole. For any given manhole, the four measurements per pickhole and individual average pickhole velocities exhibited little deviation during each sampling period.

Headspace samples were obtained by drawing known volumes of sewer gas through Carbotrap®-300 multi-bed adsorbent tubes (15 cm long, 6 mm o.d.,

stainless steel). Collection of headspace samples involved the insertion of the front end of an adsorbent tube into a pickhole, a distance of two to five centimeters below the manhole cover. A known volume of air was then drawn through the adsorbent tube using a programmable sample pump (SKC model 224-PCXR7) and pre-calibrated flow manifold. Following sample collection, each adsorbent tube was capped with teflon® ferrules and stainless steel end plugs. Tubes were then placed in a hermetically sealed glass container and kept in an ice chest while in the field. Once returned to the laboratory, all samples were refrigerated at 4 °C prior to analysis.

During Event 4, on-line TNMHC measurements were obtained with the use of a portable photoionization detector (HNU model DL-101) and data logger. Headspace gas was drawn into the detector at a rate of 225 mL/min through 6 mm o.d. teflon® tubing inserted into a pickhole.

Wastewater grab samples were drawn from the MCI to ground level through weighted, submerged 6 mm o.d. teflon® tubing. Continuous wastewater transport was performed by peristaltic pumps driven by portable generators. Grab samples were collected in 40 mL EPA-certified amber glass vials. Each sample was filled to capacity ensuring zero headspace and then sealed with teflon® lined screw caps. Wastewater samples were stored in an ice chest while in the field. Once returned to the laboratory, all samples were refrigerated at 4 °C prior to analysis.

Wastewater flowrate measurements were obtained through the use of an existing flowmeter stationed at MH3 and maintained by the Metropolitan Works Department of Toronto. Flowrates were recorded every 20 minutes.

Sample Analysis

All gas and liquid samples were analyzed within 48 hours of each field monitoring event. Specific analysis methodologies are described below.

Liquid samples which were collected during Events 5 and 6 were composited prior to analysis. Samples were then injected into a 10 mL glass sparging vessel prior to concentration on a Carbotrap®-300 adsorbent tube

connected to the vessel. The sample was purged at 100 mL/min for 10 minutes using charcoal-polished ultra-high purity (UHP) nitrogen. Previous analyses indicated that a purge volume of one liter was sufficient to remove all volatile tracers from solution without causing breakthrough of the adsorbent tube.

A sixteen-tube autosampler (Tekmar Aerotrap) was used for thermal desorption of all adsorbent tubes. The autosampler was plumbed to a purge and trap (PAT) system (Tekmar model LSC 2000) for internal concentration onto a VOCARB® 4000 focussing trap. The PAT was coupled to a gas chromatograph (GC) oven (Hewlett-Packard model 5890 series II) connected to a mass spectrometer (MS) (Hewlett-Packard model 5971).

The multi-tube autosampler method involved a 7.0 minute dry purge of each sample tube with charcoal-polished UHP helium at a rate of 100 mL/min. This was followed by a 2.50 minute sample preheat to 200 °C and sample desorption for 3.25 minutes. The focussing trap was then dry-purged at 100 mL/min for 2.50 minutes, preheated to 195 °C and desorbed for 2.50 minutes at 200 °C.

The GC was equipped with a DB-5 capillary column (30 m in length, 0.32 mm o.d., 1.0 µm film thickness). The GC was set to room temperature during desorption of the focussing trap. All lines and valve temperatures were maintained at 150 °C. The GC ramping method consisted of a constant temperature of 31 °C maintained for 2.50 minutes, ramp at 40 °C/min to 40 °C/min with a 1.0 minute hold, ramp at 9 °C/min to 200 °C with a 2.00 minute hold time.

3.3 RESULTS AND DISCUSSION

Emissions Monitoring

Outgas flowrates from four manhole covers were monitored during sampling Events 1-4. Natural ventilation of the MCI was observed to be significant as a result of the many perforated manhole covers along the segment of sewer that was studied. For Events 1, 2, and 3, combined outgas

flowrates across the four manholes of interest varied from 1300-1800 m³/h, 1300-2300 m³/h, and 1300-1600 m³/h, respectively. Thus, ranges of natural ventilation rates varied little during and between the three events, which were all completed between 8 a.m. and 4 p.m.. During Events 1-3, it was also determined that outgas flowrates generally varied by less than 35% between individual manholes.

Results of diurnal ventilation monitoring at MH3 during Event 4 are shown in Figure 3.2. Over the 24-hour period outgas flowrates at MH3 varied from a low of 140 m³/h at 6 a.m. of day 2 to a high of 590 m³/h at noon of day 1. For Events 1 through 4, outgas flowrates were consistently low in the early morning, but increased rapidly to maximum values at approximately noon. This trend was likely caused by wastewater flow patterns, i.e. peaking slightly before noon, with subsequent effects on both gas displacement by rising wastewater and changes in the influence of liquid drag on sewer gas flow.

Based on observed outgas flowrates, a range of system ventilation rates (total volume turnovers per day) was calculated. Ventilation rate estimates for Events 1, 2, 3 and 4 were 17, 19, 15, and 16 turnovers per day, respectively. These values are approximately factors of 20 to 40 greater than those reported by Pescod and Price¹² for 0.45 and 3.0 m i.d. interceptors, respectively. As a result of the highly perforated nature of manhole covers along the MCI, natural ventilation rates were likely to be higher than for most municipal sewers.

Ranges of target VOC concentrations in the MCI headspace for Events 1 through 4 are listed in Table 3.1. Benzene was generally not detected or was identified at concentration too low to quantify and thus was omitted from Table 3.1. Toluene and xylenes were the predominant target VOCs during Events 2 and 4, and toluene and ethylbenzene predominated for Event 1. Headspace concentrations of the three aromatic compounds exhibited a significant weekday/weekend trend. A similar trend was not observed for tetrachloroethene.

Variations in headspace TNMHC concentrations during Event 4 are shown in Figure 3.3. For each sampling period, the average and range of concentrations are shown for the set of four manholes. Concentration

variations between manholes were generally small. A maximum average TNMHC concentration of 95 ppm (toluene equivalents) was observed, consistent with hydrocarbon concentrations reported for sewers in Cincinnati and Sacramento (Barsky *et al.*, 1986; Huang *et al.*, 1979).

Estimated emissions for Events 1 and 2 are presented in Figures 3.4 and 3.5, respectively, for the four compounds described above. System emission rates for each compound were obtained by summing the product of ventilation rate and concentration for each manhole. As indicated by the concentration ranges in Table 3.1, emissions during Event 3 were negligible and therefore not shown graphically.

As depicted in Figure 3.4, toluene was emitted in the largest quantities for Event 1, and contributed at least 80% of total quantified target compound emissions. Emissions of toluene from the four manholes ranged from 51 to 140 g/h (450 to 1200 kg/yr). Ethylbenzene had the second highest emissions during all periods and ranged from 7 to 14 g/h (63 to 130 kg/yr). Total xylenes were relatively consistent in emissions ranging from 2.4 to 2.7 g/h (21 to 24 kg/yr), while tetrachloroethene emissions fluctuated from a low of 1.3 g/h (11 kg/yr) to a high of 4.1 g/h (36 kg/yr).

As illustrated in Figure 3.5, emission rates for all four compounds during Event 2 were lowest at 8 a.m.. Again, tetrachloroethene had the lowest emission rates for all sampling periods, ranging from 0.2 to 4.0 g/h (2 to 35 kg/yr). Emission rates for toluene varied from 6.3 to 110 g/h (55 to 940 kg/yr). Emission rates for total xylenes ranged from 8.1 to 59 g/h (71 to 520 kg/yr), while emission rates for ethylbenzene varied from 1.0 to 13 g/h (9 to 115 kg/yr).

Emission rates for toluene, ethylbenzene, total xylenes and tetrachloroethene from MH3 during Event 4 are shown in Figures 3.6 a-d. Consistent with Event 2, toluene and xylene emissions dominated over the 24-hour monitoring event. A global emission peak occurred at noon for toluene. Local emission peaks also occurred at noon for ethylbenzene and xylenes. All three aromatic VOCs exhibited peaks at 10 p.m., suggesting a night-time discharge from a common source. Tetrachloroethene emission rates were generally low, with one peak near noon consistent with a rapid slug discharge to the sewer.

Emissions of TNMHC from MH3 during Event 4 are shown in Figure 3.7. Peak emission rates ranged from 630 to 800 g/h (5500 to 7000 kg/yr) (toluene equivalents) in the afternoon. A secondary peak at 10 p.m. was consistent with those observed for the target aromatic VOCs. During GC/MS full-scan analyses, a large number of additional (non-target) VOCs were identified but not quantified. Several of these, particularly trimethylbenzene and ethyltoluene isomers were present in large quantities and likely contributed significantly to TNMHC emissions.

Comparison with Wastewater Treatment Plants

It was desired to compare VOC emissions from the MCI with those that occur at municipal wastewater treatment plants in Ontario. The plant to which the MCI eventually discharges has not been extensively studied with respect to VOC emissions. However, four other treatment plants in Southern Ontario were recently continuously-monitored over a four day period to determine summed VOC emissions from aerated grit chamber and activated sludge aeration basins (Bell *et al.*, 1988; Bell *et al.*, 1993). Measured emission rates for each plant are listed in Table 3.2. The Burlington-Skyway plant treated a mix of residential and commercial wastewater with some industrial discharge. The Highland Creek and Lakeview plants were characterized as having significant industrial flow contributions, including some from petrochemical facilities. The Waterloo plant treated primarily residential and commercial wastewater discharges. Each plant treated wastewater at flowrates that exceeded those conveyed by the MCI.

Since each of the previously-described treatment plants was monitored over four complete days, emissions were compared with those associated with MCI Event 4. Thus, integrated 24-hour emissions from MH3 are also listed in Table 3.2. Emissions from the single MCI manhole rivaled or exceeded emissions from all four treatment plants for ethylbenzene, toluene and total xylenes. Had emissions from all outgassing manholes along the MCI been accounted for, the MCI would have dominated all four plants as a source of aromatic VOC emissions. These results suggest that sewers that accept VOC-laden wastewater, and that are characterized by significant ventilation and drop

structures, can be significant sources of VOC emissions relative to municipal wastewater treatment plants.

Liquid Concentrations and Stripping Efficiencies

To determine the extent to which drop structures contribute to VOC emissions, liquid samples were collected at MH9 and MH6 (and MH3 for Event 5). Results of Event 5 indicated negligible VOC stripping along the 315 m uniform reach bounded by MH6 and MH3. Thus, only MH6 and MH9 were monitored during Event 6. As illustrated in Figure 3.1, drop structures with wastewater fall heights of approximately 3.0 and 1.4 m were located at MH8 and MH7, respectively.

Liquid concentrations for all target VOCs were greater for Event 5 than Event 6. For Event 5, the toluene concentrations in wastewater at both MH9 and MH6 were greater than 50 mg/L, values too high to accurately quantify on the GC/MS. At wastewater flowrates observed during Event 5, this lower concentration bound leads to an equivalent pure toluene discharge rate of greater than 42 L/h. Total xylene and ethylbenzene concentrations were also observed to be approximately 11 mg/L in wastewater at MH9 during Event 5. Aqueous concentrations for o-xylene, m,p-xylenes and ethylbenzene are listed in Table 3.3 for Events 5 and 6. Toluene concentrations are listed only for Event 6. Benzene and tetrachloroethene concentrations were too low to quantify.

Stripping efficiencies across the two drop structures bounded by MH9 and MH6 are also listed in Table 3.3. Stripping efficiencies varied between 29 and 44% over both events, with an average (minus toluene) of 38% for Event 5 and 33% for Event 6. Gas samples were also collected during both events as described previously. For Event 5, the system was observed to be at less than 6% of equilibrium, as defined by Henry's law, for each VOC. For Event 6, the system was observed to be between 45 and 80% of equilibrium for each VOC. This may have accounted for slightly lower stripping efficiencies for Event 6. However, gas samples were not collected continuously during either event and do not represent the entire period over which liquid samples were collected. It

is conceivable that they may have been biased by large spikes of VOC discharge during gas sampling periods. Nevertheless, stripping efficiencies at drop structures may be significantly reduced if equilibrium conditions are approached in poorly ventilated sewers. This should not have been the case during Events 5 and 6, as outgas flowrates were similar to afternoon values recorded during Events 1 through 4.

The results presented in Table 3.3 suggest that significant VOC stripping efficiencies can occur at drop structures in well-ventilated sewers. A drop structure with a 2.6 m fall height at MH10 was not monitored during this study, but would have increased overall VOC removal caused by such structures in the MCI. Thus, mass loadings in the influent streams of wastewater treatment plants may poorly represent the actual quantity of VOCs discharged to upstream sewers. The extent of this difference should be highly system-specific. Large differences are likely to occur for sewers consisting of many drop structures, and that are naturally well-ventilated or force-ventilated, e.g., for odor control.

3.4 ADDITIONAL MONITORING

Several additional monitoring events were completed in two sewer reaches located in High Park, Toronto. The results of these sampling events were not as significant, with respect to total VOC emissions, as those described above for the Massey Creek Interceptor. Nevertheless, the experimental methodologies and results associated with those sampling events are provided in detail in Volume II of this report. The reader is referred to Volume II for additional information.

3.5 SUMMARY AND CONCLUSIONS

Conditions which are conducive to high VOC emissions from sewers include 1) significant VOC discharges in the aqueous phase, 2) the presence of drop structures which enhance liquid-to-gas mass transfer, and 3) high rates of headspace ventilation. A municipal sewer that meets all three criteria was identified in Toronto, Ontario. Six monitoring events were completed on the system to determine 1) VOC emissions during weekday and weekend daytime

periods, 2) VOC emissions over a 24-hour period, and 3) VOC stripping efficiencies associated with two drop structures in series.

Important conclusions stemming from this study are:

1. A significant fraction of VOCs may be removed from wastewater and emitted to the ambient atmosphere before reaching a treatment facility. This is particularly true for well-ventilated sewers containing drop structures.
2. In accordance with conclusion 1 above, previous reports of VOC discharges to municipal sewers may be significantly underestimated, having been based on VOC mass loadings in the influent streams of wastewater treatment plants.
3. Emission "hot spots" may occur in municipal sewers at locations that meet the three conditions described above.

This study is unique in being the first to couple headspace ventilation rates and gaseous VOC concentrations to determine VOC emissions from a municipal sewer. The findings clearly suggest that, relative to wastewater treatment facilities, sewers should not be neglected as sources of VOC emissions to the ambient atmosphere, i.e., if a wastewater treatment plant is identified as a potential source of VOC emissions, its wastewater collection system may also be a significant emissions source. Sampling methodologies and results described in this paper should facilitate future studies of VOC emissions from sewers.

3.6 REFERENCES

- J.B. Barsky, S.S.Q. Hee, S. Clark, J.H. Trapp, "Simultaneous multi-instrument monitoring of vapors in sewer headspaces by several direct reading instruments," *Environmental Research*, **39**: 307 (1986).
- J.P. Bell, I. Osinga, H. Melcer, *Investigation of Stripping of Volatile Organic Contaminants in Municipal Wastewater Treatment Systems: Phase I*, Report to the Ontario Ministry of the Environment, 1988.

- J. Bell, H. Melcer, H. Monteith, I. Osinga, P. Steel, "Stripping of volatile organic compounds at full-scale municipal wastewater treatment plants," *Water Environment Research*, **65**: 708 (1993).
- D.P.Y. Chang, E.D. Schroeder, R.L. Corsi, *Emissions of Volatile and Potentially Toxic Organic Compounds from Sewage Treatment Plants and Collection Systems*, A5-127-32, California Air Resources Board, Sacramento, 1987.
- R.L. Corsi, D.P.Y. Chang, E.D. Schroeder, "A modeling approach for VOC emissions from sewers," *Water Environment Research*, **64**: 734 (1992).
- R.L. Corsi, A. Whitmore, "Municipal and industrial wastewater collection systems as sources of VOC emissions," in *Proceedings of the 9th World Clean Air Congress*, Montreal, Quebec, August 1992.
- R.L. Corsi, J. Shepherd, J. Kemp, C. Quigley, P. Martos, H. Melcer, "VOC emissions from small sewer drop structures," in *Proceedings of the 86th A&WMA Annual Meeting*, Air and Waste Management Association, June 1993.
- J.Y.C. Huang, G.E. Wilson, T.W. Schroeffer, "Evaluation of activated carbon adsorption for sewer odor control," *Journal of the Water Pollution Control Federation*, **51**: 1054 (1979).
- N.A. Jensen, T. Hvitved-Jacobsen, "Method for measurement of reaeration in gravity sewers using radiotracers," *Research Journal of the Water Pollution Control Federation*, **63**: 758 (1991).
- J.R. Mihelcic, C.R. Baillod, J.C. Crittenden, T.N. Rogers, "Estimation of VOC emissions from wastewater facilities by volatilization and stripping," *Journal of the Air and Waste Management Association*, **43**: 97 (1993).
- E. Namkung, B.E. Rittmann, "Estimating volatile organic compound emissions from publicly owned treatment works," *Journal of the Water Pollution Control Federation*, **59**: 670 (1987).
- M.B. Pescod, A.C. Price, "Fundamentals of sewer ventilation as applied to the Tyneside sewerage scheme," *Water Pollution Control*, **17** (1982).

- J.M. Reid, M. McEvoy, "Monitoring sewer atmospheres for organic vapours," *Journal of the Inst. of Water & Env. Mgmt.*, **1**: 161 (1987).
- A. Whitmore, R.L. Corsi, "Measurement of gas-liquid mass transfer coefficients for volatile organic compounds in sewers," *Environmental Progress*, **13**(2): 114 (1994).
- USEPA, *Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works*, EPA/530-SW-86-004, United States Environmental Protection Agency, Washington, D.C. (1986).

Table 3.1 Concentrations of target VOCs in the MCI (events 1-4)

Compound	Concentration (ppm)			
	Event 1	Event 2	Event 3	Event 4
toluene	8 - 18	1 - 15	ND	1 - 46
ethylbenzene	0.7 - 2	0.2 - 2	ND	ND - 5
xylene	0.3 - 0.6	1 - 7	ND	4 - 39
tetrachloroethene	0.1 - 0.4	ND - 0.3	ND - 0.2	ND - 2

ND: not detected

Table 3.2 Emission rates for the MCI and four treatment plants in Ontario

Plant Characteristics	Emissions (g/day)			
	Etbenz ^a	Toluene	Xylenes	Perc ^b
MCI (Event 4, MH3)	87	850	770	17
Burlington-Skyway ^c	30	521	129	48
Highland Creek ^d	30	269	213	61
Lakeview ^e	93	362	408	164
Waterloo ^f	0.08	2.2	0.16	17

Notes:

- a: Etbenz = ethylbenzene
- b: Perc = tetrachloroethene (perchloroethylene)
- c: 0.88 m³/s plant.
- d: 0.91 m³/s plant.
- e: 0.74 m³/s plant.
- f: 0.34 m³/s plant (primarily residential and commercial wastewater).

References for plant emissions: Bell *et al.* (1988) and Bell *et al.*, 1993

Table 3.3 Aqueous concentrations and stripping efficiencies
(MCI events 5 and 6)

Event/Compound	Aqueous Concentration (mg/L)		
	MH9	MH6	% Stripped
Event 5			
o-xylene	3.4	1.9	44
m,p-xylenes	7.7	5.0	35
ethylbenzene	11	7.0	36
Event 6			
toluene	1.7	1.2	29
o-xylene	0.37	0.23	38
m,p-xylenes	0.42	0.29	31
ethylbenzene	0.086	0.059	31

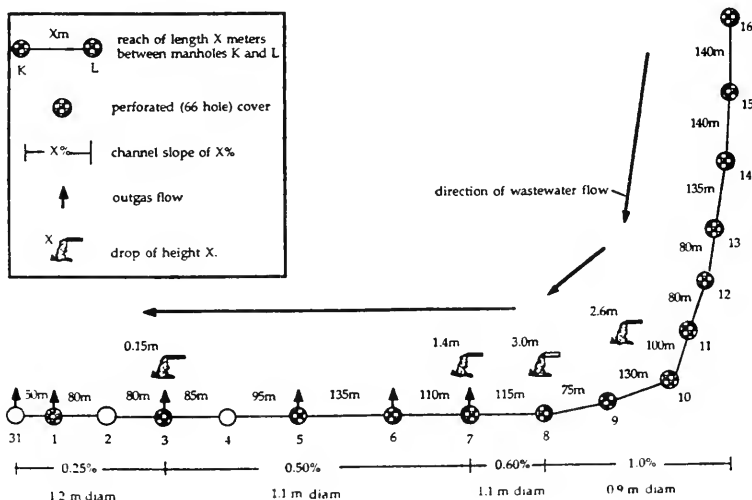


Figure 3.1 Simplified illustration of the Massey Creek Interceptor

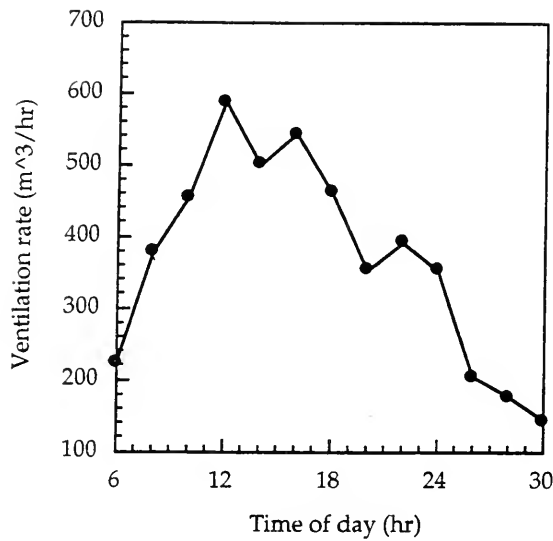


Figure 3.2 Gas flowrates exiting manhole 3 (MCI, event 4)

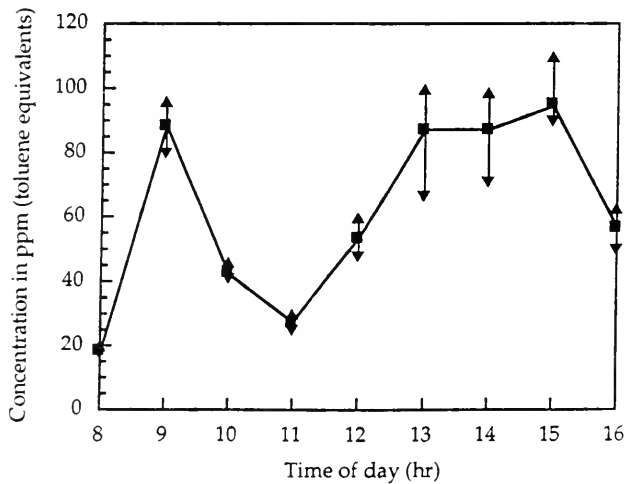


Figure 3.3 Variations in TNMHC concentration in MCI headspace (event 4)

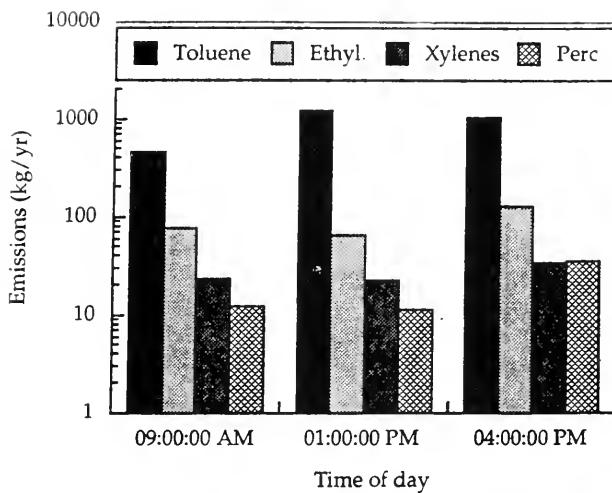


Figure 3.4 Target compound emissions from the MCI (event 1)

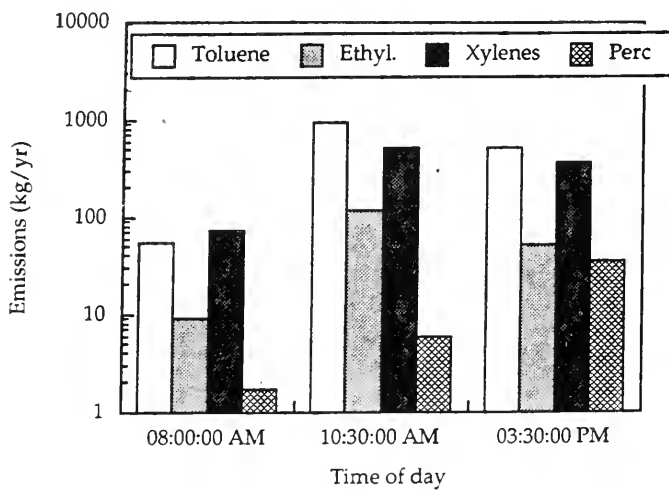
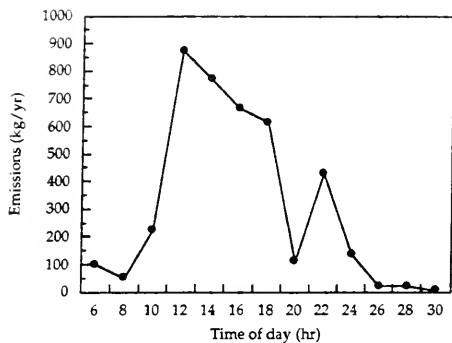
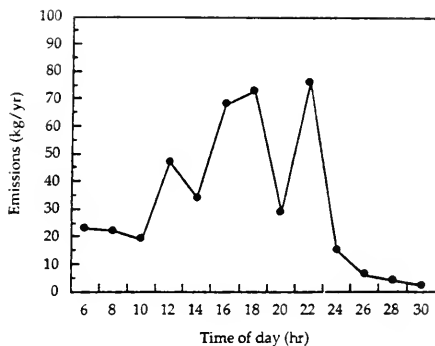


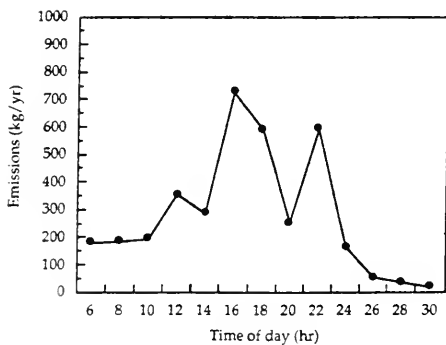
Figure 3.5 Target compound emissions from the MCI (event 2)



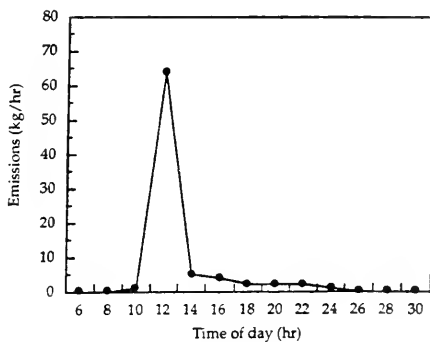
(a) toluene



(b) ethylbenzene



(c) xylenes (total)



(d) tetrachloroethene

Figure 3.6 Target compound emissions from the MCI (event 4, MH 3)

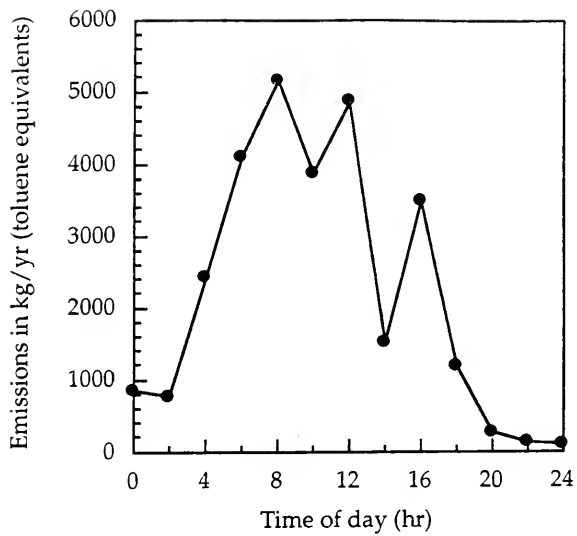


Figure 3.7 TNMHC emissions from the MCI (event 4)



Fate of Volatile Organic Compounds in Wastewater Collection Systems

Volume II: VOC Emissions from Sewers in Metropolitan Toronto

Christopher J. Quigley
M.Sc. thesis

Final Report

RAC Project No. 577G

Richard L. Corsi (principal investigator)

September, 1994



VOC EMISSIONS FROM MUNICIPAL SEWERS

A Thesis
Presented to
The Faculty of Graduate Studies
of
The University of Guelph

by
CHRISTOPHER JOHN QUIGLEY

In partial fulfilment of requirements
for the degree of
Master of Science
May, 1994

© Christopher John Quigley, 1994



ABSTRACT

VOC EMISSIONS FROM MUNICIPAL SEWERS

Chris Quigley
University of Guelph, 1994

Advisor:
Professor R.L.Corsi

Emission rates of VOCs were quantified from several operating municipal sewers. Emission rates obtained during these monitoring events were compared to previously published emission rates from four wastewater treatment plants indicating the potential for significant emissions of VOCs upstream of wastewater treatment facilities. In addition, liquid sampling events were performed in order to determine the relative significance of stripping losses across hydraulic drop structures and along a uniform section of reach. For the sewer studied, the hydraulic drop structures accounted for at least 95 % of VOC stripped. Finally, a model was developed to predict VOC stripping efficiencies across drop structures using an oxygen deficit ratio equation adjusted by a parameter used to account for compound specific gas and liquid phase resistance to mass transfer. A comparison of measured and predicted VOC stripping efficiencies across two drop structures revealed that, on average, model predictions were within $\pm 20\%$ of measured values.

TABLE OF CONTENTS

LIST OF TABLES	iv
LIST OF FIGURES	v
ACRONYMS	vii
NOMENCLATURE	viii
1. INTRODUCTION	1
1.1 RESEARCH OBJECTIVES.....	2
1.2 SCOPE OF RESEARCH	2
1.3 ORGANIZATION OF THESIS	3
2. BACKGROUND.....	4
2.1 VOLATILE ORGANIC COMPOUNDS.....	4
2.2 SOURCES OF VOC DISCHARGES TO SEWERS.....	4
2.3 CONCERNS RELATED TO VOC DISCHARGES TO SEWERS.....	5
2.4 GENERAL FATE OF VOCs IN SEWERS	5
2.5 NATURAL VENTILATION OF SEWERS.....	6
2.6 VOC CONCENTRATIONS IN SEWER HEADSPACES	8
3. VOC STRIPPING IN SEWERS.....	10
3.1 VOC STRIPPING ALONG UNIFORM REACHES	10
3.2 VOC STRIPPING AT HYDRAULIC DROP STRUCTURES.....	10
3.3 VOC STRIPPING AT HYDRAULIC DROP STRUCTURES MODEL DEVELOPMENT.....	12
4. EXPERIMENTAL METHODOLOGY:	
EMISSIONS MONITORING	20
4.1 TARGET COMPOUNDS	20
4.2 SITE SELECTION AND DESCRIPTIONS	20
4.2.1 The Massey Creek Interceptor Site.....	21
4.2.2 The High Park Site.....	25
4.3 MONITORING EVENTS	27
4.3.1 Massey Creek Interceptor Emissions Monitoring Events.....	27
4.3.2 High Park Site Emissions Monitoring Events	28
4.4 SAMPLING METHODOLOGIES	29
4.5 SAMPLE ANALYSIS	31

5. RESULTS AND DISCUSSION:	
EMISSIONS MONITORING	33
5.1 MASSEY CREEK INTERCEPTOR	33
5.1.1 Ventilation Rates	33
5.1.2 Headspace Concentrations	38
5.1.3 Emission Rate Estimates.....	47
5.2 HIGH PARK.....	54
5.2.1 Ventilation Rates	54
5.2.2 Headspace Concentrations	58
5.2.3 Emission Rate Estimates.....	64
5.3 SOURCE COMPARISON OF VOC EMISSIONS.....	68
6. EXPERIMENTAL METHODOLOGY:	
VOC STRIPPING EVENTS	72
6.1 SYSTEM DESCRIPTION.....	72
6.2 EXPERIMENTAL EVENTS.....	72
6.3 SAMPLING METHODOLOGIES	74
6.4 SAMPLE ANALYSIS	75
7. RESULTS AND DISCUSSION:	
VOC STRIPPING EVENTS	76
7.1 MCI EVENT 5	76
7.2 MCI EVENT 6	84
7.3 MODEL ASSESSMENT	85
8. RELEVANCE OF RESEARCH.....	91
9. CONCLUSIONS.....	93
10. RECOMMENDATIONS.....	95
11. REFERENCES	98
APPENDIX A:	
FLOWRATE MEASUREMENT VERIFICATION.....	101
APPENDIX B:	
MASSEY CREEK INTERCEPTOR EMISSIONS MONITORING DATA.....	105
APPENDIX C:	
HIGH PARK EMISSIONS MONITORING DATA	113
APPENDIX D:	
EMISSIONS MONITORING CALIBRATION CURVES	121
APPENDIX E:	
MASSEY CREEK INTERCEPTOR LIQUID SAMPLING EVENTS DATA	144

LIST OF TABLES

Table 4.1. Target compounds.....	20
Table 4.2 MCI Emissions Monitoring Event Summary Table	27
Table 4.3 HP Emissions Monitoring Event Summary Table.....	28
Table 5.1 Massey Creek Interceptor Events 1 - 4 time weighted average ventilation rates, concentrations and emission rates.....	37
Table 5.2 High Park Events 1 - 3 time weighted average ventilation rates, concentrations and emission rates.	57
Table 5.3 Source comparison of VOC emissions.....	70
Table 7.1 Massey Creek Event 5: Percent Stripping Results	81
Table 7.2. Event 5: Headspace Gas Degree of Saturation	84
Table 7.3 System Parameters Used in Model Predictions	86
Table 7.4 Individual and Total r_0 Values Used in Model Predictions.....	86
Table 7.5 Comparison of Predicted and Measured Percent Stripped Results	89

LIST OF FIGURES

Figure 3.1. ϕ_M vs H_C	17
Figure 4.1 General location of the Massey Creek Interceptor site.....	22
Figure 4.2 General location of the High Park site.....	22
Figure 4.3 Layout of the Massey Creek Interceptor.....	23
Figure 4.4 Daily Flowrate Pattern for the Massey Creek Interceptor.....	24
Figure 4.5 Layout of the High Park site.....	26
Figure 5.1 MCI Events 1 - 3: System Ventilation Rates.....	34
Figure 5.2 MCI Event 4: Ventilation rates at manhole 3.....	35
Figure 5.3 MCI Event 1: Target Compound Concentrations.....	39
Figure 5.4 MCI Event 2: Target Compound Concentrations.....	39
Figure 5.5 MCI Event 4: Toluene Concentrations at manhole 3.....	42
Figure 5.6 MCI Event 4: Ethylbenzene Concentrations at manhole 3.....	42
Figure 5.7 MCI Event 4: Total Xylenes Concentrations at manhole 3.....	43
Figure 5.8 MCI Event 4: Tetrachloroethene Concentrations at manhole 3.....	43
Figure 5.9 MCI Event 4: Benzene Concentrations at manhole 3.....	44
Figure 5.10 MCI Event 4: System TNMHC Concentration Variations.....	45
Figure 5.11 MCI Event 1: Target Compound Emission Rates.....	48
Figure 5.12 MCI Event 2: Target Compound Emission Rates.....	48
Figure 5.13 MCI Event 4: Toluene Emission Rates at manhole 3.....	50
Figure 5.14 MCI Event 4: Total Xylenes Emission Rates at manhole 3.....	51
Figure 5.15 MCI Event 4: Ethylbenzene Emission Rates at manhole 3.....	51
Figure 5.16 MCI Event 4: Tetrachloroethene Emission Rates at manhole 3.....	52
Figure 5.17 MCI Event 4: Benzene Emission Rates at manhole 3.....	52
Figure 5.18 MCI Event 4: TNMHC Emission Rates at manhole 3.....	53
Figure 5.19 HP Events 1 - 3: Ventilation Rates from manhole 1.....	55
Figure 5.20 HP Events 1 - 3: Combined Ventilation Rates from manholes 2 and 3.....	55
Figure 5.21 HP Event 1: Compound Concentrations at manhole 1.....	59
Figure 5.22 HP Event 2: Compound Concentrations at manhole 1.....	59
Figure 5.23 HP Event 3: Compound Concentrations at manhole 1.....	60
Figure 5.24 HP Event 1: Average Compound Concentrations at manholes 2 and 3.....	60
Figure 5.25 HP Event 2: Average Compound Concentrations at manholes 2 and 3.....	61
Figure 5.26 HP Event 3: Average Compound Concentrations at manholes 2 and 3.....	61
Figure 5.27 HP Event 1: Emission Rates from manhole 1.....	65

Figure 5.28 HP Event 1: Combined Emission Rates from manholes 2 and 3.....	66
Figure 5.29 HP Event 3: Emission Rates from manhole 1	66
Figure 5.30 HP Event 3: Combined Emission Rates from manholes 2 and 3.....	67
Figure 6.1 Liquid Sampling Locations along the MCI.....	73
Figure 7.1 Event 5 Wastewater and Headspace Ventilation Flowrates.....	77
Figure 7.2 Event 5 Ethylbenzene Concentrations at manholes 9,6, and 3.....	79
Figure 7.3 Event 5 m,p-Xylene Concentrations at manholes 9,6, and 3	79
Figure 7.4 Event 5 o-Xylene Concentrations at manholes 9,6, and 3.....	80
Figure 7.5 Event 5 Compound Wastewater Concentrations at manhole 9.....	80

GC	gas chromatograph
HWA	hot wire anemometer
HP	High Park
MCI	Massey Creek Interceptor
MDL	method detection level
MH	manhole
MOE	Ontario Ministry of Environment
MOEE	Ontario Ministry of Environment and Energy
MS	mass spectrometer
PAT	purge and trap
TNMHC	total nonmethane hydrocarbons
TPD	turnovers per day
TWAC	time weighted average concentration
TWAER	time weighted average emission rate
TWAVR	time weighted average ventilation rate
VOC	volatile organic compound
WCS	wastewater collection system
WWTF	wastewater treatment facility

The release of volatile organic compounds (VOCs) into the ambient atmosphere has recently come under close scrutiny due to the adverse environmental impacts associated with these compounds. One pathway in which VOCs are emitted into the atmosphere is through discharge of these compounds in an aqueous phase into wastewater collection systems and subsequent volatilization to overlying air. Due to the frequency of this form of disposal, the fate of VOCs in wastewater has recently drawn much attention. As a result, there has been substantial research regarding the fate of VOCs during wastewater treatment. However, there has been little research completed to determine the fate of VOCs in collection systems upstream of treatment facilities. To address this problem, in 1990, the Ontario Ministry of Environment (MOE), now the Ontario Ministry of Environment and Energy (MOEE), listed as one of its areas of research needs "Volatile Chemicals in Sewers and their Treatment". In July, 1991, the MOE awarded a three year research grant to the University of Guelph to study the fate of VOCs in sewers.

As part of the three year study, field monitoring of operating sewers was performed to assess the importance of emissions of VOCs from sewers relative to emissions of VOCs from wastewater treatment facilities. In addition, studies were conducted to identify sewer "hot spots" where the majority of stripping of VOCs from wastewater is likely to occur. These components of the three year study served as the basis for this thesis.

1.1 RESEARCH OBJECTIVES

The principle focus of this research was the study of VOC emissions from operating municipal sewers. Specifically, the research was defined by the following four objectives:

- 1) to quantify emissions of VOCs from wastewater collection systems (WCSs),
- 2) to assess the relative importance of WCSs as sources of VOC emissions to the atmosphere,
- 3) to determine WCS "hot spots" where the majority of emissions originate, and
- 4) to develop a steady state model capable of predicting VOC stripping at hydraulic drop structures within sewers.

1.2 SCOPE OF RESEARCH

Research objectives were completed within the guidelines of the following constraints:

- 1) Field monitoring of VOC emissions was limited to two sites.
- 2) Monitoring was limited to a group of ten previously selected target compounds.
- 3) The assessment of the relative importance of VOC emissions from sewers was performed by comparison of field monitoring data with previously published data regarding VOC emissions from four wastewater treatment facilities located in Ontario.
- 4) An assessment of sewer "hot spots" was limited to field monitoring at one sewer.
- 5) Development of the steady-state model was based on material previously reported in the literature. Model validation was performed by comparing predicted VOC stripping efficiencies with measured values obtained during field monitoring events.

1.3 ORGANIZATION OF THESIS

Chapter 2 contains background information regarding the use, concerns, and discharge of VOCs to sewers. In addition, factors affecting the emissions of VOCs from sewers are described. Stripping of VOCs in sewers is discussed in Chapter 3. The development of a steady-state model capable of predicting the fraction of VOC stripped at hydraulic drop structures is also presented in Chapter 3. Chapter 4 contains the field emissions monitoring events methodology. Chapter 5 contains the results and discussion of field emissions monitoring events. A comparison between VOC emissions from sewers and four wastewater treatment facilities (WWTFs) is also presented in Chapter 5. Field stripping efficiency events utilized in the study of VOC stripping at drop structures are detailed in Chapter 6. Results of field stripping efficiency events as well as a comparison between measured and model predicted results are presented and discussed in Chapter 7. The relevance of this research is discussed in Chapter 8. Conclusions and recommendations are presented in Chapters 9 and 10, respectively.

2.1 VOLATILE ORGANIC COMPOUNDS

In the most general terms, a VOC is an organic chemical which when present in aqueous solution can readily volatilize to air. One manner in which compounds are classified as VOCs is through examination of the equilibrium air/water partition coefficient known as the Henry's law coefficient (H_C). Unitless compound specific H_C values are determined by dividing equilibrium gas phase concentrations (mass / volume) by equilibrium liquid phase concentrations (mass / volume). For the purpose of this study, organic compounds with H_C values greater than or equal to $0.1 \text{ m}^3\text{liq}/\text{m}^3\text{gas}$ at 20°C will be considered to be VOCs. Examples of VOCs and their corresponding H_C value determined at 20°C obtained from Ashworth *et al.* (1988) include: benzene, $0.19 \text{ m}^3\text{liq}/\text{m}^3\text{gas}$; toluene, $0.23 \text{ m}^3\text{liq}/\text{m}^3\text{gas}$; trichloroethene, $0.35 \text{ m}^3\text{liq}/\text{m}^3\text{gas}$; and 1,1,1 - trichloroethane, $0.59 \text{ m}^3\text{liq}/\text{m}^3\text{gas}$.

2.2 SOURCES OF VOC DISCHARGES TO SEWERS

Volatile organic compounds are present in many products commonly used in the residential, commercial and industrial sectors. Examples of these products include household cleansers, degreasing solvents, products used in the dry cleaning industry, and chemicals used in certain manufacturing processes. Once used, a common form of disposal of these products is the discharge to municipal wastewater collection systems.

2.3 CONCERNS RELATED TO VOC DISCHARGES TO SEWERS

The potential for VOC emissions during both conveyance and treatment of wastewater has recently come under close scrutiny. Such scrutiny has largely been driven by knowledge of the impacts associated with these compounds. When emitted into the atmosphere, many VOCs are considered to be toxic contaminants, some of which are carcinogenic. Many of these chemicals are also highly reactive in the atmosphere and are involved in the formation of ground level ozone. These concerns have resulted in studies documenting emissions of VOCs from wastewater treatment facilities (Bell *et al.*, 1988; Dunovant *et al.*, 1986) and the development of models describing the general fate of VOCs during wastewater treatment (Blackburn, 1987; Corsi and Card, 1991; Govind *et al.*, 1991; Namkung and Rittman, 1987). While there have been no similar studies to date reporting the emissions of VOCs from sewers, emission estimation techniques for wastewater collection systems have been developed (Corsi and Whitmore, 1992).

2.4 GENERAL FATE OF VOCs IN SEWERS

After being discharged to a sewer the fates of VOCs are dependent upon the outcome of several competing removal mechanisms. There are three principle competing removal mechanisms that determine the fate of a discharged VOC: volatilization/stripping from the wastewater to overlying air, biodegradation by biomass either suspended in wastewater or attached to wetted sewer walls, and sorption of the VOC to solids that are either suspended or attached to sewer walls. The relative importance of these competing removal mechanisms is dependent on several factors including compound specific physical/chemical properties, biodegradability of the compound, the presence of suspended/attached solids and/or biomass, and wastewater flow and fluid properties.

As stated earlier, the focus of this research is on emissions of VOCs from sewers. The fate mechanism that leads to such emissions is a two step process: 1) volatilization/stripping of VOC from wastewater to an overlying sewer headspace, and 2) gas exchange between sewer and ambient atmosphere. Sewer headspace ventilation rates and gaseous concentrations of VOCs are discussed below.

2.5 NATURAL VENTILATION OF SEWERS

To date there has been limited research performed on the natural ventilation of sewers. Much of this work was undertaken because of the potential for hydrogen sulphide gas accumulation in sewer headspaces creating a health hazard for workers. The major mechanisms responsible for natural ventilation of sewers have been defined. According to Pescod and Price (1981 and 1982) there are five factors believed to play a role in sewer ventilation. These are barometric pressure gradients along sewer reaches, temperature differential between sewer and ambient atmosphere, rise and fall of wastewater level, eduction/induction of wind across sewer stacks, and induction by liquid drag.

Pescod and Price (1981) performed pilot scale studies involving a 0.3 m diameter sewer operating at various depths of flow and water flowrates and measured maximum average air velocities of approximately 0.2 m/s. They also predicted average air exchange rates ranging from 2.3 to 0.5 volumetric turnovers per day (TPD) for operating sewers ranging in size from 0.45 to 3.0 m diameter, respectively. Volumetric turnovers per day were defined as gas flowrate divided by total sewer volume.

Thistlethwayte (1972) reported that air velocity exiting a 3200 m section of sewer ranging in diameter from 0.6 to 2.7 m ranged between 1.0 to 2.0 m/s. However, neither air flowrate or area of flow was measured preventing a calculation of TPD. In addition,

Thistlethwaite (1972) described an Australian study in which it was determined that natural ventilation of 5 to 7 ft (1.5 to 2.1 m) diameter sewers could result in ventilation rates of approximately 16 TPD.

Corsi *et al.* (1989) used theoretical fluid dynamics to investigate the relative importance of the ventilation mechanisms described by Pescod and Price (1981). They concluded that gas mean velocities in sewers should rarely exceed 0.25 m/s, and suggested that sewer ventilation rates likely range from less than one to twenty five TPD.

Due to the limited research performed in this area one common assumption made when estimating VOC emissions from sewers is that of infinite ventilation. The validity of this assumption depends on several factors including compound specific H_C values and the number and size of system openings. For systems with many openings (e.g., vent stacks, highly perforated manholes) the potential for extensive air exchange is possible and an infinite ventilation assumption may be valid. Corsi *et al.* (1993) simultaneously solved gas and liquid phase mass balances for an enclosed drop structure resulting in the formulation of the following relationship:

$$\frac{C_2}{C_1} = \frac{1}{1 + K_L a \theta_H f} \quad (1)$$

and

$$f = 1 - \frac{1}{\frac{Q_g H_C}{V K_L a} + 1} \quad (2)$$

where

C_1 = upstream concentration of VOC in liquid, (mg/m³);

C_2 = tailwater concentration of VOC in liquid, (mg/m³);

K_L = liquid-based overall mass transfer coefficient for a VOC, (m/hr);

a = specific area defined as area/volume, (1/m)

θ_H = hydraulic residence time in the tailwater, (hr);

f = ventilation factor

Q_g = headspace ventilation rate, (m^3/hr);

H_c = compound Henry's law coefficient, (m^3_{liq}/m^3_{gas});

V = tailwater volume, (m^3).

The percentage of chemical stripped can be calculated using the formula $(1 - C_2/C_1) \times 100$. It is evident from equation 1 that the amount stripped is dependent on the ventilation factor f . The value of f ranges between zero and one representing conditions of no ventilation and infinite ventilation, respectively. Examination of equation 2 reveals the dependence of f on both system operating conditions and compound properties. For situations with $Q_g H_c$ high relative to $V K_L a$ an assumption of infinite ventilation may be valid.

2.6 VOC CONCENTRATIONS IN SEWER HEADSPACES

To date there have been at least three published reports of measured VOC concentrations in sewer headspaces.

Huang *et al.* (1979) reported total organic compound concentration data obtained in the headspace of a main interceptor in Sacramento, California. Samples were collected on four different days and had total organic concentrations varying from 13 to 531 ppm. In all samples analyzed, an eight carbon compound with a boiling point of 160 °C was present in the highest amount ranging from 31 to 83 percent of the total by volume.

Barsky *et al.* (1986) monitored five sewers for organic vapors in Cincinnati, Ohio. In all samples saturated aliphatic organics were the dominant group. Of the five sewers

monitored, two served chemical producing plants, two received effluent from various sectors and one served a residential area. The latter three sewers contained less than 3 ppm of total organic compounds reported as benzene equivalents. The two sewers conveying effluent from the chemical plants had concentrations ranging from 0 to 64 ppm (benzene equivalents).

Reid and McEvoy (1987) monitored several sewers in London, England, in a study designed to compare different VOC headspace concentration measurement techniques. Their study included the monitoring of six sites along four different sewers, each receiving various amounts of industrial effluent. Measurements in a sewer receiving low levels of industrial discharge indicated the presence of hexane, cyclohexane, toluene, p-xylene and tetrachloroethene. Concentration levels ranged from 1.0 ppm for tetrachloroethene to 18 ppm for hexane. In another sewer receiving significantly more industrial effluent, a total of 10 VOCs were detected with concentrations greater than 0.5 ppm. Detected compounds included: tetrachloroethene (1.1 ppm), ethylbenzene (1.2 ppm), p-xylene (2.8 ppm), chlorobenzene (12 ppm), chloroform (15 ppm), dichlorobenzenes (17 ppm), benzene (49 ppm), trichloroethene (107 ppm), and toluene (168 ppm). Three sites were monitored along a sewer known to receive high levels of toluene. Concentrations ranged from a low of 10 ppm, measured at the furthest downstream site, to a high of 150 ppm recorded at the site closest to the point of discharge. In addition, liquid samples were collected to allow for a comparison between actual headspace concentrations and those predicted based on Henry's law. At both sites where liquid sampling was performed it was determined that, on average, actual headspace concentrations were 79% of predicted values. Reid and McEvoy also performed a 24 hour sampling event in which 12 two hour samples were collected in another sewer. Results from this field study demonstrated large temporal variation in concentrations. A total of seven VOCs were quantified. Concentrations ranged from 0.1 to 1.1 ppm for nonane and 29 to 153 ppm for toluene.

The ability to estimate VOC emissions from sewers requires knowledge regarding VOC gas-liquid mass transfer and sewer ventilation rates. For sewers that are well ventilated and subsequently have little or no gaseous VOC accumulation, emissions are solely related to the gas-liquid mass transfer rate. There are two general locations along sewers where gas-liquid mass transfer is known to occur: 1) along sewer reaches characterized by uniform flow, and 2) at points along sewers such as hydraulic drop structures where there is a rapid change in potential energy.

3.1 VOC STRIPPING ALONG UNIFORM REACHES

Whitmore and Corsi (1992) performed field tracer experiments in two operating municipal sewers in Guelph, Ontario in order to calculate gas-liquid mass transfer coefficients for uniform flow conditions. Experimentally derived mass transfer coefficients were then used to predict the length of uniform reach required to achieve various percentage removals of VOC from the liquid phase by stripping. Three experiments were performed in one sewer having a slope of 0.1%, diameter of 1.2 m, and an average wastewater flowrate of $0.11 \text{ m}^3/\text{s}$. Using these results it was predicted that to strip approximately 5% of 1,1,1-trichloroethane it would require, on average, lengths of sewer exceeding 1 km.

3.2 VOC STRIPPING AT HYDRAULIC DROP STRUCTURES

To date, there have been no reported stripping rates of VOCs from operating sewer hydraulic drop structures. Pincince (1991) assessed the relative importance of emissions from primary clarifier weirs at wastewater treatment plants with respect to emissions from

aerated grit chambers, clarifier surfaces, and aeration tanks. He predicted that VOC losses across primary weirs should generally exceed both aerated grit chambers and clarifier surfaces. Emissions of highly biodegradable VOCs were also predicted to be higher at weirs than aeration tanks.

Corsi *et al.* (1993) performed several pilot drop structure experiments designed to study the effects of system operating conditions on emissions. Operating conditions varied during the experiments included: drop height, liquid flowrates, and headspace ventilation rates. Several compounds were also used during each experiment to determine the effects of compound physicochemical properties on stripping. For the range of operating conditions and chemicals tested, stripping efficiencies ranged from less than 1% to over 30%.

As an initial estimate of the relative importance of stripping at drops versus stripping along uniform reaches a comparison of results of percent stripping at these two locations for 1,1,1-trichloroethane was performed. As stated earlier, Whitmore and Corsi (1992) predicted for one sewer studied approximately 1 km of uniform sewer reach was needed to strip 5%. In the pilot drop experiments performed by Corsi *et al.* (1993), 1,1,1-trichloroethane stripping averaged 19%. Although it is possible that the conditions analyzed for each location represented extreme conditions the comparison suggests that stripping from drop structures may dominate uniform sewer reaches.

Based on this observation, a steady state empirical model capable of predicting stripping of VOCs across well ventilated drop structures was developed and is presented below.

3.3 VOC STRIPPING AT HYDRAULIC DROP STRUCTURES: MODEL DEVELOPMENT

Most work regarding mass transfer at drop structures has been focused on studying the potential for reaeration of water and wastewater. One parameter commonly referred to when discussing water and wastewater reaeration is the oxygen deficit ratio (r_o), which describes dimensionlessly the change in dissolved oxygen across any two locations. Mathematically the deficit ratio is defined as:

$$r_o = \frac{C_{1o} - \frac{C_{go}}{H_{co}}}{C_{2o} - \frac{C_{go}}{H_{co}}} \quad (3)$$

where:

r_o = oxygen deficit ratio;

C_{1o} = upstream dissolved oxygen concentration, (mg/m³);

C_{2o} = downstream dissolved oxygen concentration, (mg/m³);

C_{go} = drop structure gaseous oxygen concentration, (mg/m³);

H_{co} = Henry's law coefficient for oxygen, (m³liq/m³gas).

Many researchers have empirically related r_o to various system operating parameters (Apted and Novak, 1973; Avery and Novak, 1978; Nakasone, 1986). Selection of the operating parameters used to predict r_o requires knowledge of the various mechanisms involved in oxygen mass transfer at drop structures. Nakasone (1986) stated that mass transfer could occur at three different locations within the drop structure: 1) at the gas-liquid surface of the

falling nappe, 2) between tailwater and air bubbles entrained at the plunge point of the falling jet, and 3) at the agitated tailwater surface. The relative importance of each mechanism depends upon specific operating conditions. Nakasone (1986) derived a set of empirical equations relating r_0 to four system operating parameters for weirs. The parameters that he selected were: 1) drop height, 2) tailwater depth, 3) liquid discharge rate per unit width of weir and 4) depth of flow on weir. The general form of the empirical equation is:

$$\ln r_{20} = a(D+1.5H)^b q^c T^d \quad (4)$$

where:

r_{20} = oxygen deficit ratio at 20 °C;

D = drop height, (m);

H = depth of flow on weir, (m);

q = weir discharge rate per unit width, (m³/m hr);

T = tailwater depth, (m).

The values of the constants a , b , c and d are dependent on q and D as presented in Table 3.1.

Table 3.1 Equation 4 constant values.

System operating conditions		Constants			
q (m ³ /m hr)	D (m)	a	b	c	d
≤ 235	≤ 1.2	0.0785	1.31	0.428	0.310
≤ 235	> 1.2	0.0861	0.816	0.428	0.310
≥ 235	≤ 1.2	5.39	1.31	-0.363	0.310
≥ 235	> 1.2	5.92	0.816	-0.363	0.310

To account for temperature effects on r_o , Nakasone suggested using the following experimentally derived equation:

$$\ln r_T = \ln r_{20} [1 + 0.0168 (T - 20)] \quad (5)$$

Gas-liquid mass transfer of VOCs can also be described by a VOC deficit ratio (r_{voc}) similar to the oxygen deficit ratio defined earlier as:

$$r_{voc} = \frac{C_1 - \frac{C_g}{H_c}}{C_2 - \frac{C_g}{H_c}} \quad (6)$$

where:

r_{voc} = VOC deficit ratio;

C_1 = upstream liquid VOC concentration, (mg/m^3);

C_2 = downstream liquid VOC concentration, (mg/m^3);

C_g = headspace VOC concentration, (mg/m^3);

H_c = Henry's law coefficient for VOC, ($\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$).

As an alternative to equation 6, r_{voc} can be estimated from r_o by the following relationship:

$$r_{voc} = r_o^\phi \quad (7)$$

and

$$\varphi = \left(\frac{K_{lvoc}}{K_{lo}} \right)^n \quad (8)$$

where:

φ = ratio of VOC and oxygen overall mass transfer coefficients;

K_{lvoc} = liquid based overall mass transfer coefficient for a VOC, (m/hr);

K_{lo} = liquid based overall mass transfer coefficient for oxygen, (m/hr);

n = adjustment exponent ranging from 0.5 to 1.

The value of n used depends on which mass transfer theory is used to represent two phase mass transfer. Use of two film theory results in a value of 1 for n , while use of surface renewal/penetration theory results in n equal to 0.5 (Dobbins, 1962). The overall mass transfer coefficient can be mathematically described by:

$$\frac{1}{K_{lvoc}} = \frac{1}{k_{lvoc}} + \frac{1}{k_{gvoc} Hc} \quad (9)$$

where

k_{lvoc} = liquid phase mass transfer coefficient for a VOC, (m/hr);

k_{gvoc} = gas phase mass transfer coefficient for a VOC, (m/hr);

$1/K_{lvoc}$ = overall resistance to mass transfer for a VOC, (hr/m);

$1/k_{lvoc}$ = liquid phase resistance to mass transfer for a VOC, (hr/m);

$1/k_{gvoc} Hc$ = gas phase resistance to mass transfer for a VOC, (hr/m).

A simplifying assumption that is often made is that k_{gvoc}/k_{lvoc} is very large (i.e. greater than 100) and that for compounds with Hc greater than 0.1 it is therefore possible to

neglect gas phase resistance to mass transfer (McLachlan *et al.* 1990). Using this information and simplifying Equation 9 it can be shown that K_{lvoc} can be approximated by k_{lvoc} . Substitution of the following mathematical definition of k_{lvoc} :

$$k_{lvoc} = \frac{D_{lvoc}}{d} \quad (10)$$

into Equation 6 results in:

$$\phi = \left(\frac{D_{lvoc}}{D_{lo}} \right)^n \quad (11)$$

where

D_{lvoc} = liquid phase molecular diffusion coefficient for a VOC, (m^2/hr);

d = liquid film thickness, (m);

D_{lo} = liquid phase molecular diffusion coefficient for oxygen, (m^2/hr);

$n = 1$ (from two film theory).

One major drawback to the use of Equations 7 and 11 in predicting r_{voc} from r_o is that Equation 11 is based on the assumption that gas phase resistance to mass transfer is negligible. While this assumption may be valid for systems in which there is a high degree of turbulence and mixing in the gas phase resulting in a small gas film thickness and subsequent low gas phase resistance to mass transfer, it may not be valid for systems in which air entrainment is present. It is expected that there is not a high degree of turbulent motion within entrained air bubbles and that k_{gvoc} should be lower than observed in other systems. Thus, omission of gas phase resistance to mass transfer in determining K_{lvoc} could significantly increase the value of ϕ used in Equation 5.

To address this concern, Hsieh *et al.* (1992) performed bench scale diffused bubble aeration experiments in which they estimated k_g/k_l ratios for different operating conditions. Results from their experiments indicated that for specific conditions, k_g/k_l ranged between 2.2 and 3.6. In addition, Hsieh *et al.* derived an alternative factor ϕ_M to be used for ϕ . Mathematical development of ϕ_M included both gas and liquid phase resistances. Data reported by Hsieh *et al.* were used in this study to develop a relationship between ϕ_M and H_c . The relationship is illustrated in Figure 3.1.

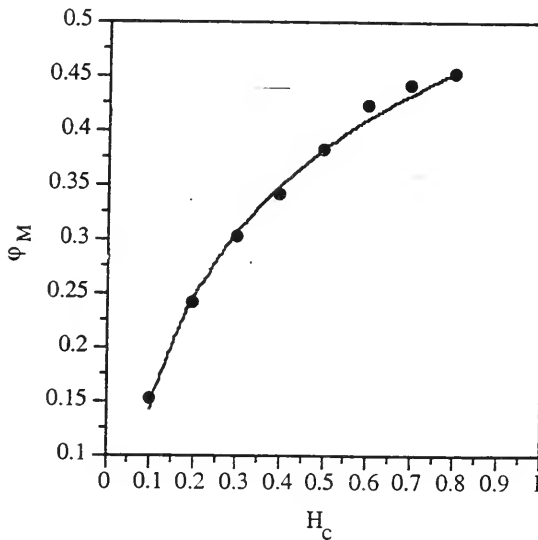


Figure 3.1 ϕ_M vs. H_c .

The best-fit curve drawn through the data points in Figure 3.1 is based on the following equation:

$$\phi_M = 0.15 \ln (H_c) + 0.486 \quad (12)$$

Nakasone (1986) observed that greater than 95% of oxygen mass transfer at drop structures was attributable to entrained air bubbles. Based on this observation and work by Hsieh *et al.*, Equation 7 was modified resulting in:

$$r_{\text{voc}} = r_{\text{O}}^{\phi_{\text{M}}} \quad (13)$$

If the system being modeled is well ventilated, Equations 6 and 13 can be used to predict the percent stripped that occurs over a drop for any given VOC. Using either measured r_{O} or predicted values of r_{O} obtained through Equation 5 and a value for ϕ_{M} calculated with Equation 12, r_{voc} can be determined. For systems that are well ventilated there should be insignificant accumulation of compound in the gas phase. Thus, the terms $(C_1 - C_g/Hc)$ and $(C_2 - C_g/Hc)$ in Equation 6 to be approximated by C_1 and C_2 , respectively. Upon simplification, Equation 6 becomes:

$$r_{\text{voc}} = \frac{C_1}{C_2} \quad (14)$$

In general, the percent stripped across a drop structure is defined as:

$$\% \text{ Stripped} = \left(1 - \frac{C_2}{C_1} \right) 100 \quad (15)$$

The percent stripped across a drop structure can then be calculated using the following formula, by substitution of r_{voc} from Equation 14 into Equation 15:

$$\% \text{ Stripped} = \left(1 - \frac{1}{r_{\text{voc}}} \right) 100 \quad (16)$$

Utilization of Equation 16 allows for the estimation of emissions from drop structures under the worst case scenario in which the sewer is assumed to be well ventilated.

4. EXPERIMENTAL METHODOLOGY: EMISSIONS MONITORING

4.1 TARGET COMPOUNDS

In consultation with the MOE steering committee a group of ten target compounds was selected for field monitoring. This list is presented in Table 4.1. These compounds were selected because they are frequently detected in influent streams to wastewater treatment plants and also because they are included in the Ontario Environmental Monitoring Priority Pollutant List.

Table 4.1. Target compounds

Benzene
Chlorobenzene
Chloroform
1,4-Dichlorobenzene
Ethylbenzene
Tetrachloroethene
Toluene
1,1,1-Trichloroethane
Trichloroethene
Xylenes (all isomers)

4.2 SITE SELECTION AND DESCRIPTIONS

With the assistance of the Metropolitan Works Department of Toronto, two field sites were selected for VOC emissions monitoring. Site selection was based on the following criteria:

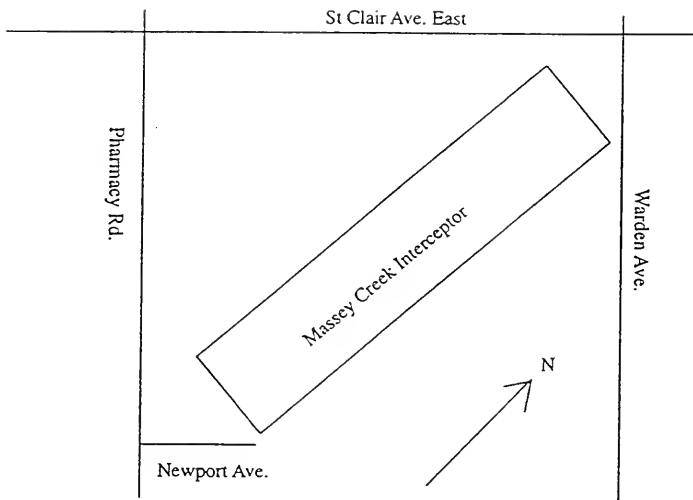
- 1) The site-associated WCS conveyed significant amounts of solvent-laden industrial wastewater.
- 2) The site had a history of solvent based odours.
- 3) The site was easily accessible and isolated from traffic.

The first two criteria were used in order to identify sewers believed to represent worst case situations with respect to VOC emissions. Emissions monitoring of these sewers were not performed to quantify emissions from "average" sewers. Monitoring worst case sewers would allow for the determination if any sewer might have potentially high emissions of VOCs relative to other emissions sources, particularly wastewater treatment facilities.

The first site which was studied included a section of the Massey Creek Interceptor (MCI) located in Scarborough, east of Toronto proper. The second site was in High Park (HP), west of downtown Toronto. General locations for the Massey Creek Interceptor site and the High Park site are presented in Figures 4.1 and 4.2, respectively.

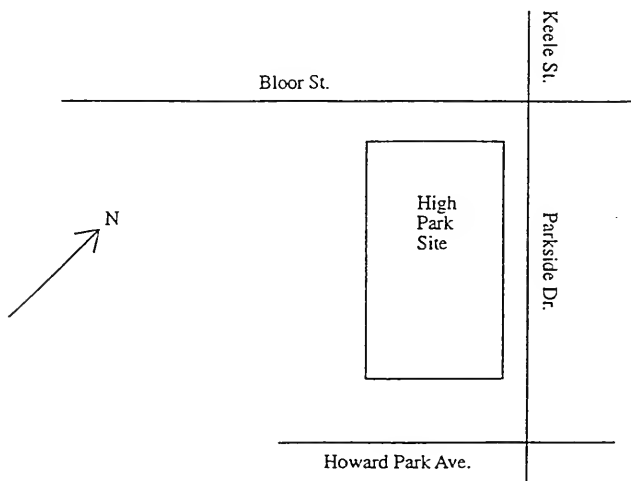
4.2.1 The Massey Creek Interceptor Site

A schematic of the MCI is presented in Figure 4.3. The section of the MCI selected for field monitoring was approximately 1600 m in length, containing 17 manholes, each separated by approximately 100 m. Fourteen of the seventeen manholes located along the MCI had highly perforated covers (i.e. containing 66 pickholes). Channel slopes and pipe diameters ranged from 0.25 to 1.0% and 0.9 to 1.2 m respectively. Four drops were located along the MCI and ranged from 0.15 to 3.0 m in height.



Drawing not to scale

Figure 4.1 General location of the Massey Creek Interceptor site.



Drawing not to scale

Figure 4.2 General location of the High Park site.

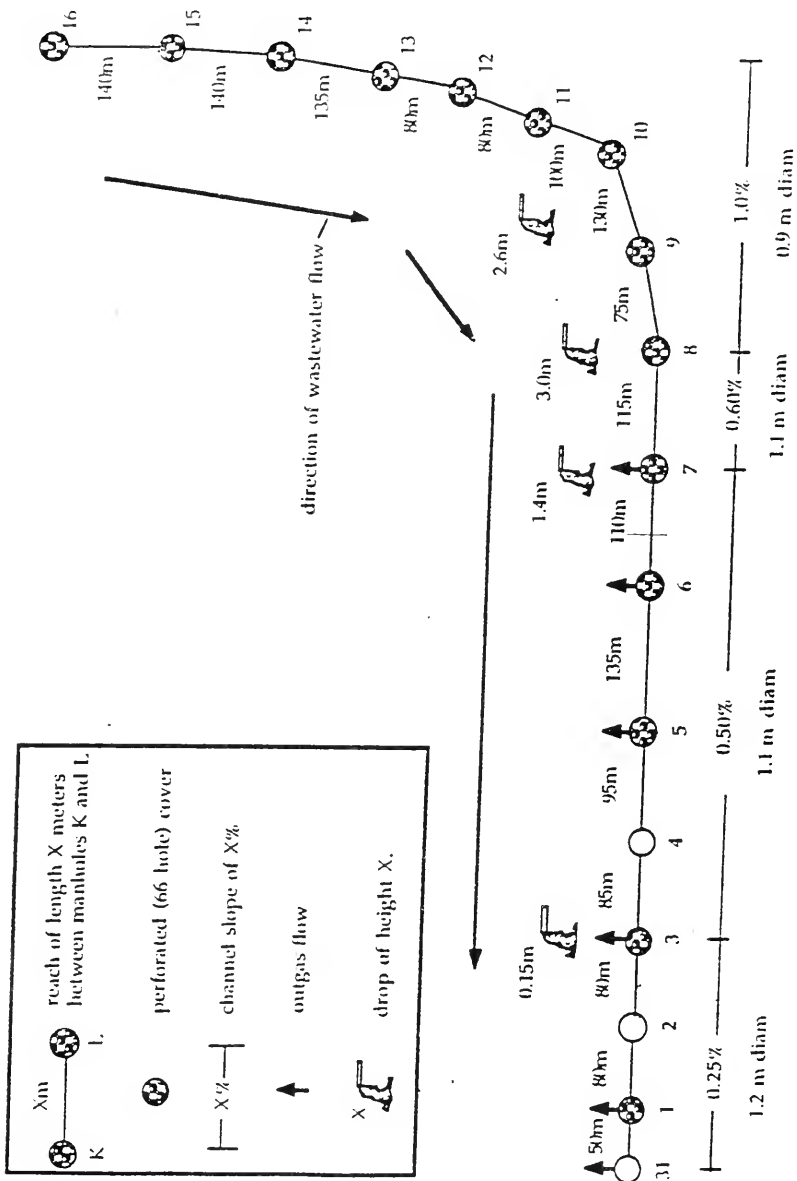


Figure 4.3 Layout of the Massey Creek Interceptor

Figure 4.4 presents average wastewater flowrate vs time of day for the MCI. Data used to generate this figure were recorded at fifteen minute intervals at MH3 between February 25 to March 3, 1992. The MCI was determined to have an average daily flowrate of approximately $0.18 \text{ m}^3/\text{sec}$.

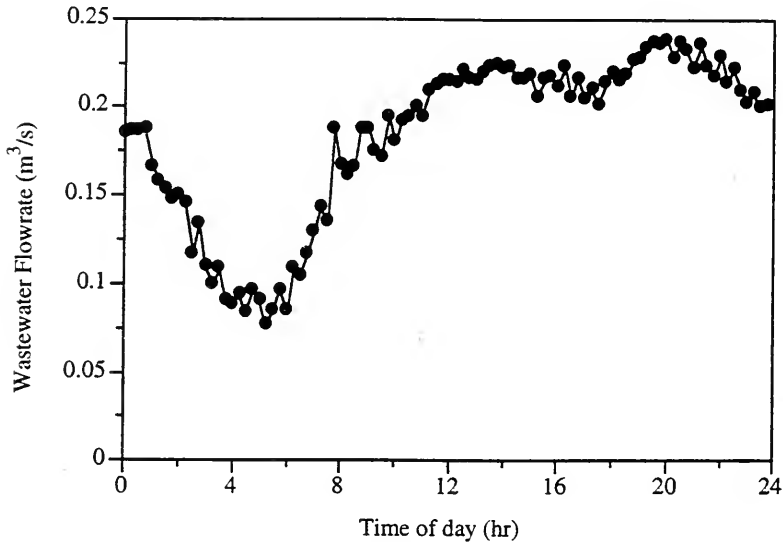


Figure 4.4 Daily Flowrate Pattern for the Massey Creek Interceptor.


A preliminary reach inspection was performed prior to sampling to determine exact locations for emissions monitoring. This field survey indicated that the downstream section of the MCI bounded by manholes 7 and 31 (MH7, MH31) contained manholes through which the majority of outgassing occurred. In this section, five of the eight manhole covers were highly perforated. Only one of the two-pickhole covers, the manhole cover located at MH31, appeared to have significant outgassing.


To ascertain the relative importance of emissions between covers with two and those with 66 pickholes, ventilation rate and headspace samples were measured/collected at manhole 31 and manhole 1. Emissions from the highly perforated cover exceeded those from the two pickhole cover by between one and two orders of magnitude. Based on this finding, it was decided to limit emissions monitoring at the MCI to only highly perforated manhole covers.


4.2.2 The High Park Site

The High Park site (Figure 4.5) encompassed an area containing two sewers operated by either the Metropolitan Works Department of Toronto or the City of Toronto Works Department. Central to the selection of this site was the presence of a large junction box located on a sewer maintained by the Metropolitan Works Department of Toronto. Ventilation of the junction box was performed by two exhaust vents. In addition to these vents there were several highly perforated manhole covers located along the two sewer reaches.

A preliminary site inspection revealed that, in an effort to curtail the odourous emissions from the junction box, both exhaust vents had been plugged with charcoal filled bags. Also, many of the highly perforated manholes had been replaced with two pickhole covers in order to restrict sewer ventilation at these locations. It was determined that there were only three highly perforated manhole covers, located on the two separate sewer lines, with significant outgassing in the immediate area. One of the highly perforated manhole covers was located on a 1.2 m diameter sewer maintained by the Metropolitan Works Department of Toronto while the other two were located on a 1.8 m diameter line maintained by the

 66 pickhole cover

 2 pickhole cover

 junction box vent

 MH 2

City reach
1.8 m diam.

wastewater flow

MH 3

Drawing not to scale

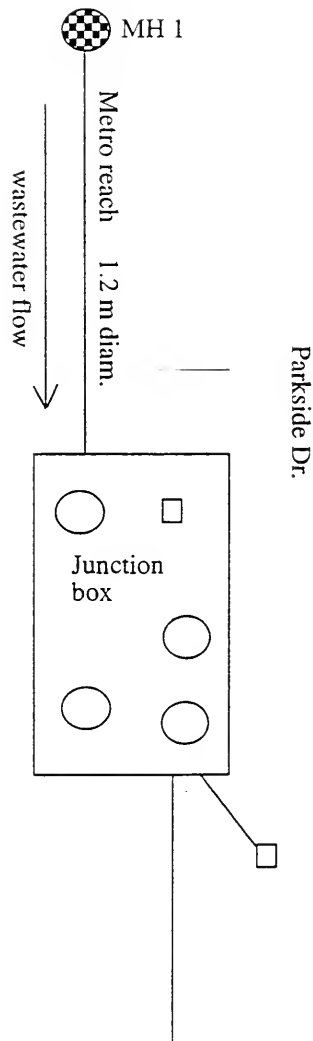


Figure 4.5 Layout of the High Park site.

City of Toronto Works Department. Therefore, emissions monitoring at High Park focussed on these three manhole covers.

During High Park Event 2, the presence of another two highly perforated manhole covers located on the City of Toronto sewer reach were identified. Monitoring of these additional manhole covers was subsequently included in High Park Event 3.

4.3 MONITORING EVENTS

4.3.1 Massey Creek Interceptor Emissions Monitoring Events

Four monitoring events were completed on the MCI. The dates and duration of each event are presented in Table 4.2.

Table 4.2 MCI Emissions Monitoring Event Summary Table

Event	Date	Day	Duration (hrs)
1	August 26, 1992	Wednesday	7
2	September 3, 1992	Thursday	7.5
3	November 8, 1992	Sunday	7
4	July 22, 1993	Thursday	24

For the first three events, headspace gas samples and outgassing flow rates were measured at MH7, MH6, MH5 and MH3. For Event 1, headspace samples were collected at 9:00, 1:00 and 16:00, and outgassing flow rates were measured at 9:00, 11:00, 13:00, 15:00 and 16:00. Headspace samples were collected during Event 2 at 8:00, 10:30 and 15:30. Outgassing flow rates for Event 2 were measured at 8:00, 9:15, 10:30, 11:45, 13:30, 14:15 and 15:30. For Event 3, headspace samples were collected and outgassing flow rate measurements were recorded at 9:00, 13:00 and 16:00. During each sampling period,

samples were first collected/measured at the furthest upstream manhole (MH7). The remaining manholes were then sequentially sampled in the direction of wastewater flow.

During Event 4, headspace gas samples were collected only at MH3. Headspace sampling was performed every two hours for the 24-hour period beginning at 6:00. Outgassing flow rates from MH3 were measured at 6:00, 8:00 and then hourly until 20:00, followed by measurements at 22:00, 0:00, 2:00, 4:00 and 6:00.

Measurements to determine total nonmethane hydrocarbon (TNMHC) concentrations were also performed at MH3 at these times. In addition, TNMHC and outgassing flow rates were measured at MH7, MH6 and MH5 at 6:00, 8:00 and then hourly until 16:00.

4.3.2 High Park Site Emissions Monitoring Events

Three monitoring events were completed. The dates and duration of each event are presented in Table 4.3.

Table 4.3 HP Emissions Monitoring Event Summary Table

Event	Date	Day	Duration (hrs)
1	June 25, 1993	Friday	7.5
2	June 27, 1993	Sunday	7.5
3	June 30, 1993	Wednesday	7.5

As discussed previously, three highly perforated manhole covers were monitored during all three events. Gas sample collection/outgassing measurements were consistently performed in the following order: 1) MH1 (located on the Metropolitan Works Department of Toronto line); 2) MH2 (located on the City of Toronto Works Department line); and 3) MH3 (located downstream of MH2).

During all three events sample collection and outgassing flowrate measurements were performed at 8:00 and then every 90 minutes until 15:30 resulting in six samples and six ventilation measurements per location. During Event 3 two additional manholes, MH4 and MH5, located on the City of Toronto Works Department line were monitored for emissions at the 9:30, 12:30, and 14:00 sampling periods.

4.4 SAMPLING METHODOLOGIES

Estimation of speciated VOC emissions for all emissions monitoring events required the acquisition and analysis of headspace gas samples and the measurement of outgassing flow rates. Determination of TNMHC emissions during MCI Event 4 necessitated additional TNMHC concentration measurements. Associated sample methodologies are described below.

Outgassing Flow Rate Measurements. A hot wire anemometer was used to obtain sewer gas effluent velocities. Readings were taken with the anemometer probe flush with the manhole cover. At each manhole, velocity measurements were recorded along a traverse diameter including between three and seven pickholes. Measurements were repeated four times for each pickhole. An average velocity was then calculated and used in conjunction with the measured total area of all pickholes to obtain a flow rate per manhole. For any given manhole cover, individual average pickhole velocities were very similar (i.e. within $\pm 10\%$) during each sampling period. A comparison of this flow measurement technique was performed in the laboratory with the following two techniques; a concentration dilution method and a timed volume displacement method. Results of this comparison are presented in Appendix A and validate its use in the field as a flowrate measurement method.

Sewer Headspace Sampling. Headspace samples were obtained by drawing known volumes of sewer gas through Carbotrap-300 Multi-bed Adsorbent Tubes (15 cm long, 6 mm o.d., stainless steel). Collection of headspace samples involved the insertion of the front end of an adsorbent tube into a pickhole a distance of two to five centimeters below the manhole cover. A known volume of air (approximately 30 mL obtained over a one minute interval) was then drawn through the adsorbent tube using a programmable sample pump (SKC model 224-PCXR7). Pumps and manifolds were precalibrated in the laboratory using a bubble flowmeter. Following sample collection, each adsorbent tube was capped with Teflon ferrules and stainless steel end plugs. Tubes were then placed in a hermetically sealed glass container and kept in an ice chest while in the field. Once returned to the laboratory, all samples were refrigerated at 4° C prior to analysis. After analysis, individual flowrates were measured for each tube. This was accomplished through the operation of the sample pump, manifold and adsorbent tube assembly in the laboratory in a manner identical to field conditions. Individual trap flowrates were measured using a bubble flowmeter connected to the sample pump exhaust port.

Before each sampling event adsorbent tubes were cleaned by simultaneous baking at 325°C for two hours and purging with ultra high purity nitrogen at a volumetric flowrate between five and ten mL/min. One adsorbent tube from every batch cleaned was analyzed to ensure all tubes were clean prior to field monitoring.

During several monitoring events sample duplicates were collected and breakthrough analyses were performed. Duplicate sample analysis indicated good reproducibility of results (i.e. $\pm 15\%$) while breakthrough traps contained less than 5% of mass contained on primary sample tubes. In addition, field blanks were routinely taken. Analysis of the field blank traps revealed no quantifiable contamination.

Total Nonmethane Hydrocarbon Analysis. On-line TNMHC concentration measurements were obtained with the use of a portable photoionization detector (HNU model DL-101). Headspace gas was drawn into the detector through Teflon tubing inserted into a pickhole at a flow rate of 225 mL/min. Total nonmethane hydrocarbon concentrations, expressed in toluene equivalents (ppm by volume), were both displayed and recorded in the detector data logger for later retrieval.

4.5 SAMPLE ANALYSIS

A sixteen-tube Tekmar Aero autosampler was used for thermal desorption of all adsorbent tubes. The autosampler was connected to a purge and trap (PAT) system (Tekmar model LSC-2000) for internal concentration onto a VOCARB 4000 focussing trap. The PAT was coupled to a gas chromatograph (GC) oven (Hewlett Packard model 5890 series II) connected to a mass spectrometer (MS) (Hewlett Packard model 5971).

The autosampler method involved a 7.0 minute dry purge of each sample tube with UHP charcoal polished helium at a rate of 100 mL/min. This was followed by a 2.50 minute sample preheat to 200 °C and sample desorption for 3.25 minutes. The focussing trap was then dry-purged at 100 mL/min for 2.50 minutes, preheated to 195 °C and desorbed for 2.50 minutes at 200 °C.

The GC was equipped with a DB-5 capillary column (30 m in length, 0.32 mm o.d., 1.0 µm film thickness). The GC was set to room temperature during desorption of the focussing trap. All lines and valve temperatures were maintained at 150 °C. The GC ramping method consisted of a constant temperature of 31 °C maintained for 2.50 minutes, ramp at 40 °C/min to 40 °C with a 1.0 minute hold, ramp at 9 °C/min to 200 °C with a 2.00 minute hold time.

The MS detector was optimally tuned for bromofluorobenzene and all samples were analyzed in scan mode.

Commercial standard mixtures (Supelco VOC mixes 7 and 8) were used to develop three-to-four point external calibration curves for each target compound. Calibration curves were characterized by R^2 values between 0.932 and 0.999.

5.1 MASSEY CREEK INTERCEPTOR

5.1.1 Ventilation Rates

During both the preliminary site visit and all sampling events at the MCI significant outgassing was observed at manholes 3, 5, 6 and 7. Although the physical cause for the outgassing at these locations was not investigated, one possible explanation is offered. There is a junction box located at manhole 31 in which the MCI joins another reach. It is possible that at the entrance of the junction box there is some form of physical obstruction in the sewer headspace creating an increased resistance to gas flow in the same direction as the wastewater. As a result of this resistance, the headspace gas flows out through other paths of lower resistance which are located at the highly perforated manhole covers located between manholes 7 and 1.

System ventilation rates measured during Events 1, 2 and 3 are presented in Figure 5.1. Event 4 ventilation rates were measured at MH3 every two hours and are presented in Figure 5.2. Ventilation rate measurements taken during Events 1 to 4 are presented in tabular form in Appendix B Table B.1 (Note: From now on any table number preceded by a letter is located in the appendices; e.g. Table C.3 refers to the third table located in Appendix C). System ventilation rates were obtained by summing the ventilation rates measured at each individual manhole cover. System ventilation rates for the first three events ranged from 1,300 to 2,300 m³/hr. Statistical analysis of data containing ventilation measurements at all four manholes during Events 1 to 4 revealed that, on average, MH3 contributed approximately 24% of total system ventilation. Use of this average, which had

a coefficient of variation of 15%, enabled extrapolation of ventilation rates from MH3 to other manholes during Event 4. Subsequently, system ventilation rates were predicted to range from 600 to 2,200 m³/hr.

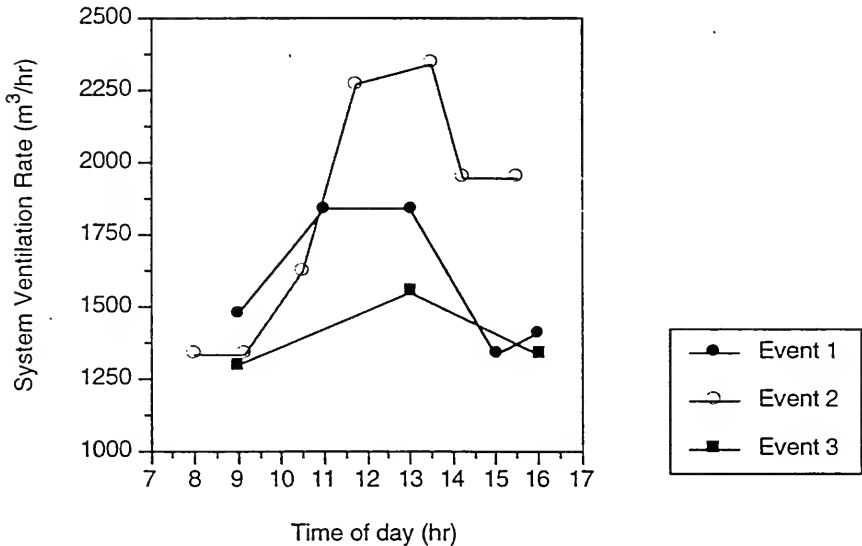


Figure 5.1. MCI Events 1 to 3: System Ventilation Rates.

Time weighted average ventilation rates (TWAVR) for each event are presented in Table 5.1, and range from a low of 34,000 m³/day for the weekend event (Event 3) to 45,000 m³/day during the week (Event 2). The average system ventilation rate and coefficient of variation for all four events were 39,000 m³/day and 12 %, respectively, indicating a relatively consistent ventilation rate for all four events. System ventilation rates, in terms of turnovers per day (TPD), are presented in Table 5.1 and ranged from 26 TPD (Event 3) to 34 TPD (Event 2). It should be noted that ventilation measurements obtained during Events 1 through 3 were taken over a maximum of seven sampling periods during an eight

hour time interval. There is therefore the possibility that the TWAVR calculated using these measurements were not representative of average ventilation rates for those events.

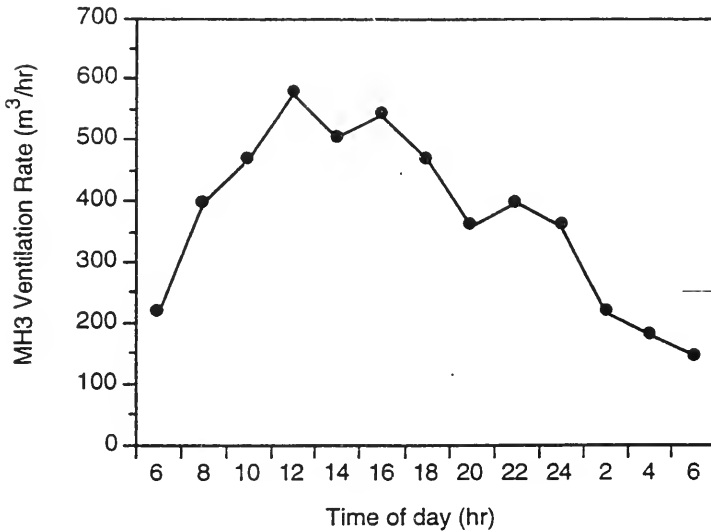


Figure 5.2 MCI Event 4: Ventilation rates at manhole 3.

Calculation of TPD was performed by assuming that all outgassing from the 1600 m section of the MCI studied occurred between MH7 and MH3. Alternatively, it is possible to describe the system ventilation rate with respect to liquid flowrate. Using Event 4 ventilation data and liquid flowrate data, a ratio of Q_{air}/Q_{ww} can be obtained where Q_{air} and Q_{ww} are the ventilation and liquid flowrates, respectively. Event 4 Q_{air} and Q_{ww} values were 37,000 m³/day and 15,500 m³/day (0.18 m³/s), respectively, resulting in $Q_{air}/Q_{ww} = 2.4 \text{ m}^3_{air}/\text{m}^3_{ww}$. In addition, if the depth of wastewater flow is known it is possible to calculate v_{air}/v_{ww} where v_{air} and v_{ww} are the average headspace gas and wastewater

velocities, respectively. Knowledge of the depth of flow allows for the calculation of both the gas and liquid cross sectional area of flow, and subsequently an average velocity for each fluid. It was determined that for Event 4, $v_{air}/v_{ww} = 0.43 m_{air}/m_{ww}$. It is believed that as a means of presenting system ventilation rate information both the Q_{air}/Q_{ww} and v_{air}/v_{ww} ratios are superior to the TPD value as they are related to measurable wastewater flow parameters. Values for Event 1 through 4 Q_{air}/Q_{ww} and v_{air}/v_{ww} ratios are presented in Table 5.1. These values were estimated using historical average daily wastewater flowrate data as actual liquid flowrate data were not available.

During Events 1 through 3 MCI system ventilation rates increased with time from the first monitoring period to around noon. The ventilation rates then leveled off to values roughly equal to or slightly higher than rates measured during the morning. In Event 4 the same trends were observed with the addition of a marked decrease in ventilation after midnight.

Ventilation patterns can probably be best explained in relation to wastewater flowrate patterns. Because ventilation is directly related to wastewater flow through the induction of air flow by liquid drag it is expected that as wastewater flowrates increase, ventilation rates should also increase. Comparing the ventilation rates of Events 1 through 4 presented in Figure 5.1 and 5.2 with the wastewater flowrate data contained in Figure 4.4 reveals that the measured ventilation rates follow the same general trends as wastewater flowrate.

Ventilation rates measured during Event 3, the weekend event, did not change much with time compared to the three weekday events. This may be due to different wastewater flowrate patterns between weekday and weekend.

Table 5.1 Massey Creek Interceptor Events 1 - 4 time weighted average ventilation rates, concentrations and emission rates.

	Event 1	Event 2	Event 3	Event 4
<u>Ventilation Rate</u> (m ³ /day)	39,500	45,000	34,300	37,000
TPD	30	34	26	28
Q _{air} /Q _{ww} (m ³ _{air} /m ³ _{ww})	2.5	2.9	2.2	2.4
V _{air} /V _{ww} (m _{air} /m _{ww})	0.45	0.52	0.39	0.43
<u>Concentration</u> (mg/m ³)				
Toluene	66	44	BMDL	81
Ethylbenzene	5.8	5.1	BMDL	9.1
Total Xylenes	1.8	26	BMDL	79
Tetrachloroethene	1.2	0.9	1.1	1.4
Benzene	ND	ND	ND	8.5
<u>Emissions</u> (g/day)				
Toluene	2500	1800	< 2.5	3800
Ethylbenzene	220	209	< 2.5	390
Total Xylenes	67	1010	< 2.5	3400
Tetrachloroethene	48	40	35	78
Benzene	ND	ND	ND	350

BMDL: Below method detection limit (< 0.1 mg/m³)

ND: Non detect.

The calculated TPD for all four MCI events were an order of magnitude greater than rates predicted by Pescod and Price (1981) but were only slightly higher than the upper bound values predicted by Corsi *et al.*, (1989). Ventilation rates measured at the MCI were probably not representative of all sewers due to the presence of numerous highly perforated manhole covers. Also, the calculation was based on an assumption that only the 1600 m

section of the MCI was ventilated through the manholes studied. It is possible that the section of the MCI ventilated at these manholes was longer than 1600 m. If this were the case, then the estimated TPDs for all events would be lower than presently predicted.

While inspection of the ventilation results indicates the usefulness of the anemometry based ventilation measurement method there are several sources of potential error which need to be addressed. To accurately quantify the system ventilation rate based on outgassing flowrates it is necessary to identify and measure all outgassing sites. It is also important that the anemometer be positioned during measurements such that horizontal winds moving across the manhole do not directly influence the reading. It is imperative that sufficient readings be taken at different locations on the manhole to ensure that an appropriate average velocity is used in conjunction with the total area of outgassing in the calculation of the outgassing flowrate. It is expected that the measured individual manhole ventilation rates are within $\pm 20\%$ of the actual value. Finally, in order to get an accurate TWAVR using this form of measurement it is necessary that sufficiently numerous measurements be taken to ensure that any temporal variations in ventilation rates are included.

5.1.2 Headspace Concentrations

Four of the target compounds (toluene, ethylbenzene, total xylenes, and tetrachloroethene) were identified and quantified during all sampling periods of Events 1 and 2. System average concentrations during each sampling period for all detected compounds are presented in Figures 5.3 and 5.4. Calibration curves used in the quantification of target compounds are presented in Appendix D. Individual compound concentrations measured at each manhole during events 1 and 2 are presented in Tables B.2 and B.3.

Concentrations

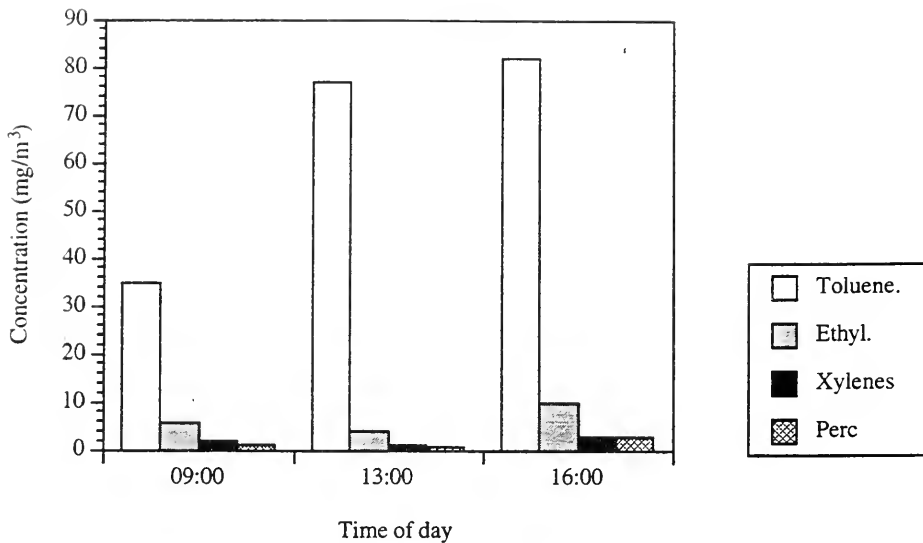


Figure 5.3 MCI Event 1: Target Compound Concentrations.

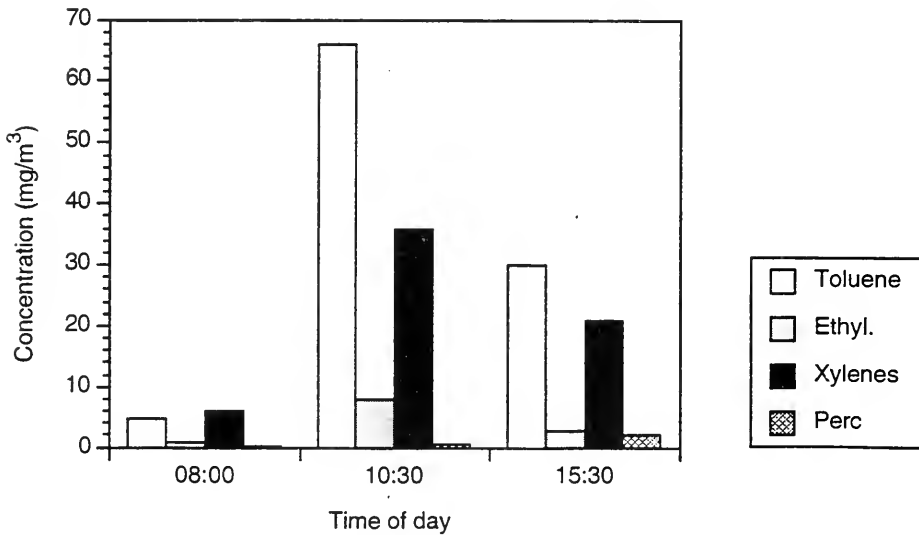


Figure 5.4 MCI Event 2: Target Compound Concentrations.

for total xylenes in Event 1 were expressed in terms of ethylbenzene equivalents as xylene standards were unavailable.

During Event 1, tetrachloroethene was present in the lowest concentrations, ranging from 0.1 mg/m³ at 13:00 to 2.9 mg/m³ at 16:00. Tetrachloroethene was followed in increasing concentration by total xylenes, ethylbenzene, and toluene, with ranges of 1.3 to 2.8 mg/m³, 3.9 to 10 mg/m³, and 37 to 82 mg/m³, respectively. The highest concentration for all four compounds were measured at 16:00.

For each sampling period in Event 2, tetrachloroethene was again present in the lowest concentrations, ranging from 0.1 mg/m³ at 8:00 to 2.0 mg/m³ at 15:30. Ethylbenzene had the second lowest average concentrations ranging from 0.8 to 8.0 mg/m³. Total xylene concentrations ranged from 6.1 to 36 mg/m³. Toluene was present in the highest concentrations and ranged from 4.7 to 66 mg/m³. The lowest system average concentration for toluene, total xylenes and ethylbenzene occurred at 8:00, while the highest concentration for each of these compounds occurred at 10:30.

All compounds except tetrachloroethene were below the method detection limit (0.1 mg/m³) for all sampling periods during Event 3. Tetrachloroethene was detected at two of four manholes at 9:00 and at all four manholes at the 13:00 and 16:00 sampling periods. System average concentrations ranged from 0.2 mg/m³ to 1.7 mg/m³. Tetrachloroethene concentrations at individual manholes are presented in Table B.4.

Target compounds detected and quantified during Event 4 were the same as those detected during Events 1 and 2 with the exception that benzene was also detected during Event 4. Concentrations of toluene, ethylbenzene, total xylenes, tetrachloroethene and benzene measured at MH3 during 13 sampling periods are presented in Figures 5.5 to 5.9 and in

Table B.5. Standard curves used in calculating sample concentrations were the curves used for High Park Events 1 to 3, and are contained in Appendix D. The use of these curves was verified by a mid-point calibration.

For Event 4, toluene concentrations ranged from a low of 3.6 mg/m^3 observed during the last sampling period, to a high of 176 mg/m^3 at 14:00. With the exception of the 20:00 sampling period, toluene concentrations between 12:00 and 22:00 were at least 120 mg/m^3 . Between 22:00 and 6:00 of the following day, concentrations were at least a factor of two lower than during the 12:00 to 22:00 time period. At 10:00, 12:00, 14:00 and 18:00, toluene had the highest concentration relative to all other target compounds.

Ethylbenzene concentrations ranged from 1.9 mg/m^3 during the last sampling period to 22 mg/m^3 at 22:00. Similar to toluene, ethylbenzene concentrations were significantly lower after the 22:00 sampling period.

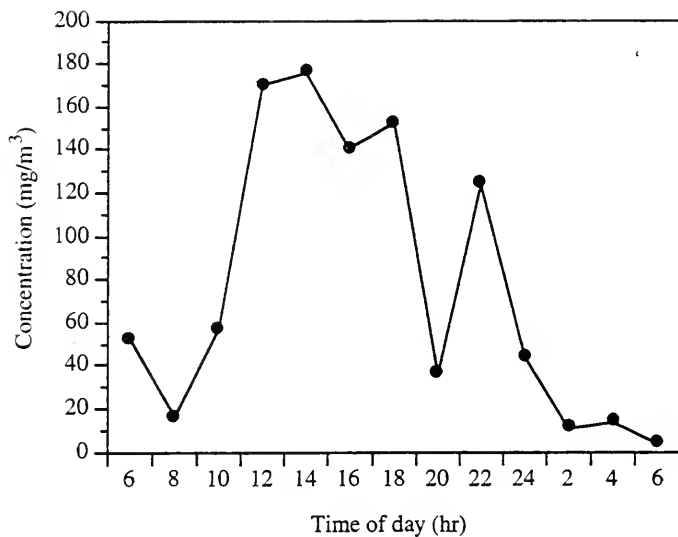


Figure 5.5 MCI Event 4: Toluene Concentrations at manhole 3.

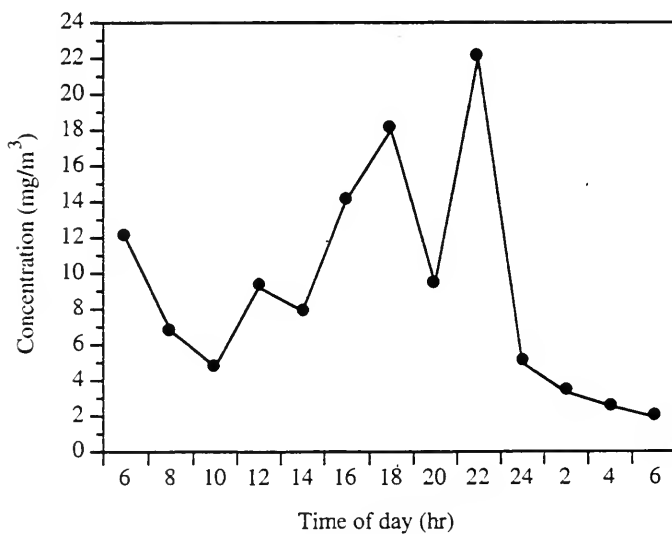


Figure 5.6 MCI Event 4: Ethylbenzene Concentrations at manhole 3.

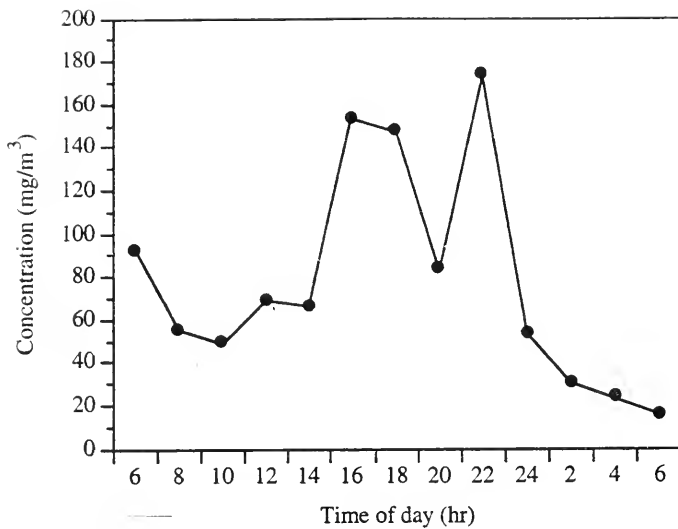


Figure 5.7 MCI Event 4: Total Xylenes Concentrations at manhole 3.

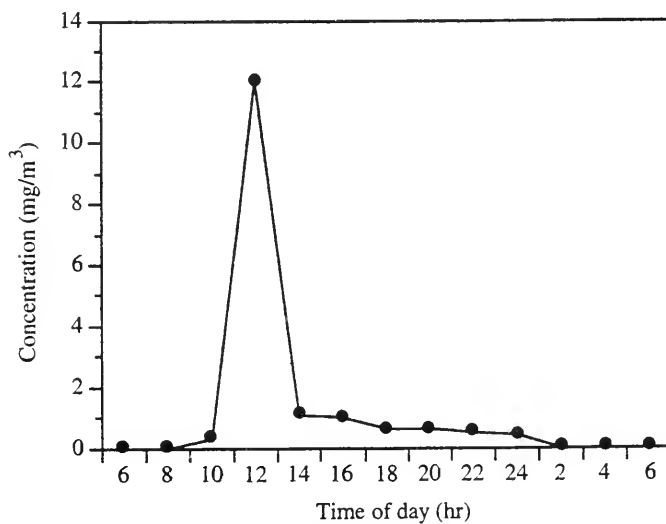


Figure 5.8 MCI Event 4: Tetrachloroethene Concentrations at manhole 3.

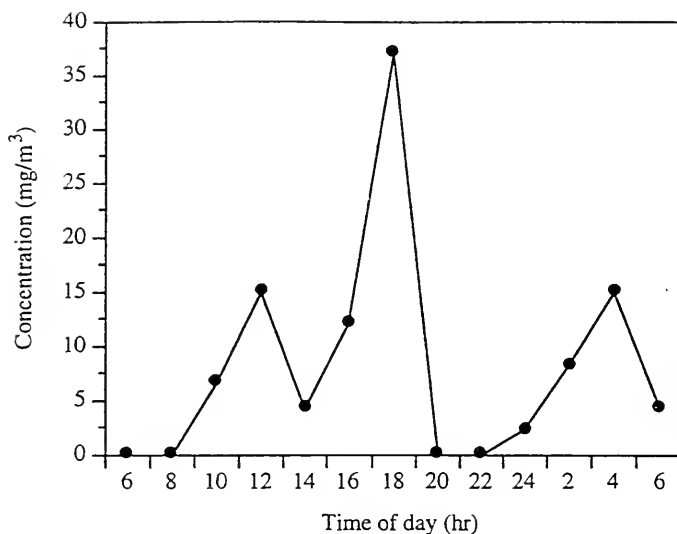


Figure 5.9 MCI Event 4: Benzene Concentrations at manhole 3.

The general trends for the total xylenes were similar to those for ethylbenzene. Low and high concentrations were 15 and 173 mg/m³ during the last sampling period and 22:00, respectively. With the exception of four sampling periods; 10:00, 12:00, 14:00 and 18:00, total xylenes had the highest measured concentrations.

Tetrachloroethene concentrations are presented in Figure 5.8 and ranged from non-detect to 12 mg/m³. Only one sample, 12 mg/m³ at 12:00, had concentrations of tetrachloroethene significantly greater than 1 mg/m³.

Concentrations of benzene are presented in Figure 5.9, and ranged from non-detect to 37 mg/m³. One significant difference between benzene and the other aromatic hydrocarbons is the peak of benzene present at 4:00. Concentrations of toluene, ethylbenzene and the total xylenes all decreased between the 18th and 24th hour of sampling.

In addition to the sampling for target compounds at MH3 during Event 4, total TNMHC concentrations were measured at MH7, MH6, MH5 and MH3 hourly from 8:00 to 16:00. The average and range of TNMHC concentrations at each time for the four manholes are presented in Figure 5.12. Individual manhole TNMHC concentrations at each measurement time are presented in Appendix B Table B.6. System average TNMHC concentrations ranged from a low of 18 ppm toluene equivalents (69 mg/m³) at 8:00 to a high of 96 ppm toluene equivalents (366 mg/m³) at 15:00. The variability of TNMHC concentrations between manholes at any given time was low and never exceeded 15% of the average value.

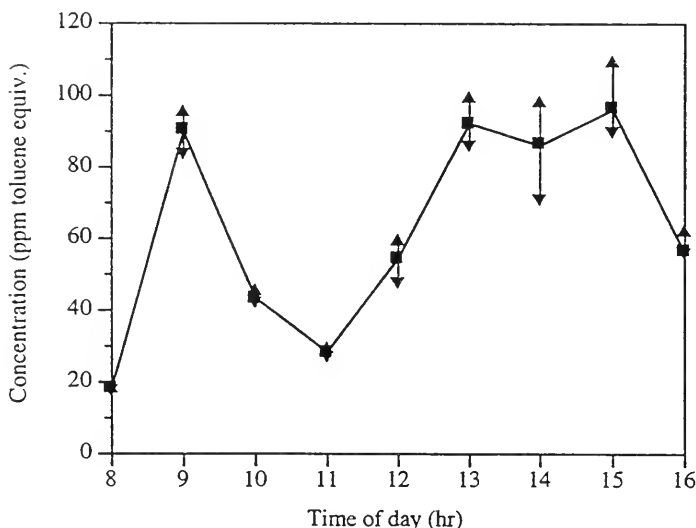


Figure 5.10 MCI Event 4: System TNMHC Concentration Variations.

Time weighted average system concentrations (TWAC) for target compounds detected during each event are presented in Table 5.1. Tetrachloroethene was the only target compound quantified during all four events and had TWAC between 0.9 and 1.4 mg/m³.

Benzene was only detected during Event 4 and had a TWAC of 8.5 mg/m^3 . Toluene, ethylbenzene and total xylenes were quantified during Events 1, 2 and 4, and ranged from 44 to 81 mg/m^3 , 5.1 to 9.1 mg/m^3 , and 1.8 to 79 mg/m^3 , respectively.

The most important observation made during Events 1 through 4 was the presence of high temporal variability in target compound concentrations. Large fluctuations were possible over small time intervals. For example, the average system concentration of toluene during Event 2 jumped from approximately 15 mg/m^3 at 8:00 to over 60 mg/m^3 at 10:30. This could be most easily explained by a noncontinuous discharge of compounds at the source. The range of TNMHC concentrations measured at the four manholes during Event 4 and presented in Figure 5.12 indicate a relatively low variability in spatial concentrations along the MCI.

For Events 1 and 2, concentrations tended to be lowest during early morning sampling and were higher later in the day. During Event 2, the three aromatic compounds had lowest and highest concentrations at the same times suggesting a potential link with respect to sources. The presence of tetrachloroethene and absence of the aromatic compounds during Event 3 indicates that there were at least two sources which discharged VOCs.

The case for a potential link between toluene, ethylbenzene and the xylenes is further strengthened by the data collected during Event 4. All three compounds had relatively low concentrations at 8:00, generally increased until 18:00, had lower levels at 20:00, peaked again at 24:00 and then tailed off with time. Because benzene is usually associated with toluene, ethylbenzene and the xylenes in mixtures commonly referred to as BTEX, the presence of all four groups suggests a common source. However, this was not likely the case during Event 4, as benzene concentrations increase during the period from 22:00 to 4:00 (following morning) while the other three compounds decrease in concentration. The

appearance of the high concentration of tetrachloroethene at 12:00 followed by lower concentrations during Event 4 suggests that discharge of tetrachloroethene was short in duration and traversed the MCI in a pulse like pattern.

It is important to state that TWAC for Events 1 through 3 were based on only three sampling periods which when taken together may not accurately represent the true TWAC for the entire event. Event 4 TWAC estimates were based on 13 different samples and, with respect to the first three events, probably better represent the actual TWAC present during Event 4.

In addition, determination of individual sample concentrations is susceptible to error. Errors in the quantification of total volume collected per tube and/or the amount of mass of compound present by analysis using GC/MS would lead to the incorrect determination of the actual concentration present. Based on the potential for errors associated with sampling and analysis it is expected that estimated concentrations are approximately $\pm 25\%$ of the actual concentration.

It is suggested that to improve the determination of TWAC it is necessary to either collect grab samples more frequently or collect samples over longer times. An increase in collection time could be accomplished through the use of either Tedlar bags or stainless steel cannisters, both of which allow filling over sustained time periods (e.g. several hours).

5.1.3 Emission Rate Estimates

System emission rate estimates for Events 1 and 2 are presented in Figures 5.11 and 5.12, and in tabular form in Tables B.2 and B.3. Emission rate estimates for each compound

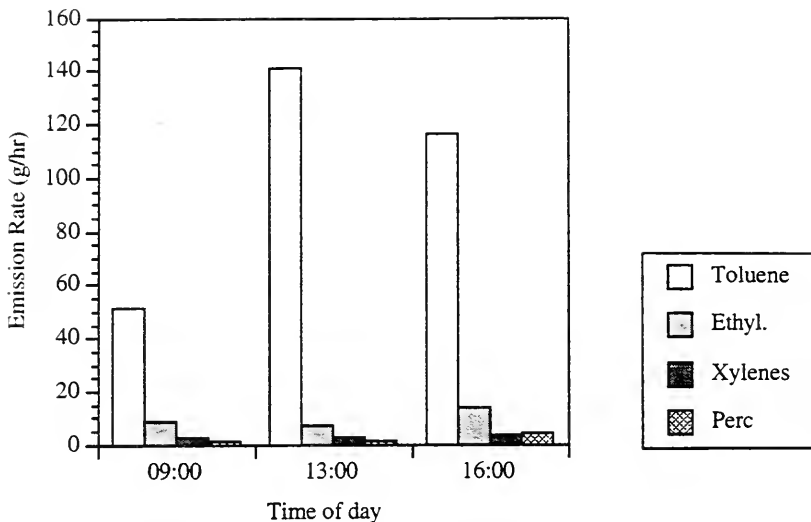


Figure 5.11 MCI Event 1: Target Compound Emission Rates.

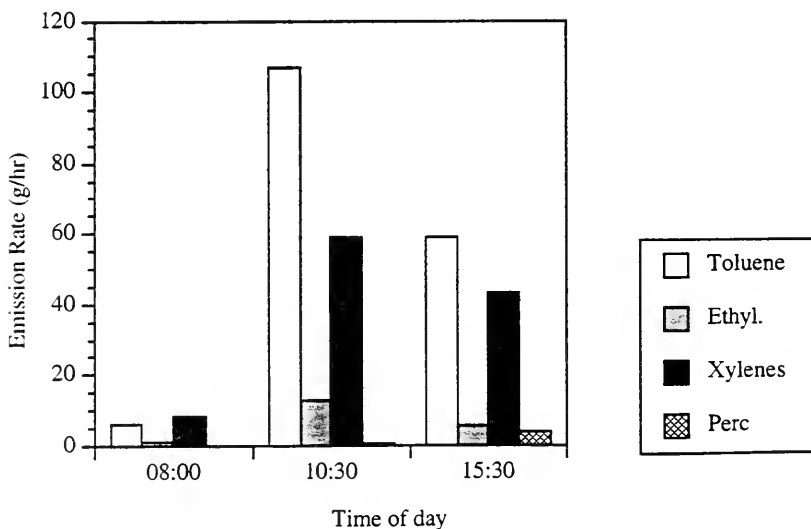


Figure 5.12 MCI Event 2: Target Compound Emission Rates.

were obtained by summing the product of ventilation rate and concentration for each manhole.

As shown in Figure 5.11, toluene was emitted in the largest quantities, and contributed at least 80% of total quantified target compound emissions. System emission rates of toluene ranged from 51 g/hr at 9:00 to 129 g/hr at 13:00. Ethylbenzene had the second highest emission rate during all periods and ranged from 7.2 to 14 g/hr. Total xylenes were relatively consistent in emissions and varied between 2.4 and 3.9 g/hr. Tetrachloroethene emissions fluctuated between 1.4 and 4.2 g/hr. Ethylbenzene, total xylenes and tetrachloroethene had low and high emission rates at 13:00 and 16:00, respectively.

As illustrated in Figure 5.12, system emission rates during Event 2 were lowest at 8:00. Again, tetrachloroethene had the lowest emission rates for all sampling periods, ranging from 0.2 to 4.0 g/hr. In addition to a common period of low emission rates, all three aromatic compounds had highest rates at 10:30. Emission rates of toluene varied from 6.3 to 106 g/hr. Emission rates for total xylenes ranged from 8.3 to 52 g/hr, while emissions of ethylbenzene varied from 1.1 to 13 g/hr.

Because concentrations of toluene, ethylbenzene and total xylenes during Event 3 could not be quantified, upper bound emission rates for these compounds were calculated. This was achieved by assuming that each compound was present at a concentration equal to the MDL. The MDL was then coupled with the TWAVR to estimate worst case emissions, resulting in maximum emission rates less than 0.1 g/hr. Tetrachloroethene was detected at all three sampling periods and had system emission rates ranging from 0.2 g/hr at 9:00 to 2.2 g/hr at 4:00. Tetrachloroethene system emission rates are presented in Table B.4.

Emission rates for the five target compounds detected at MH3 during Event 4 are presented in Figures 5.13 to 5.17 and in Table B.5. With the exception of tetrachloroethene and benzene, emissions of the detected target compounds could be quantified during all 13

sampling periods. As in Events 1 and 2, Toluene (Figure 5.13) had the highest emission rates and ranged from a low of 0.65 g/hr to a high of approximately 100 g/hr. Next in magnitude were the total xylenes (Figure 5.14) which varied from 2.0 to 83 g/hr. Ethylbenzene emissions (Figure 5.15) ranged from 0.2 to 8.7 g/hr, while emissions of tetrachloroethene, as presented in Figure 5.16, were centered mainly around a large spike of 7.3 g/hr at 12:00. Benzene emissions from MH3 are presented in Figure 5.17 and were as high as 17 g/hr. The lowest emission rates for toluene, ethylbenzene and the total xylenes occurred during the last sampling period. With the exception of ethylbenzene which had peak emissions at 22:00, all detected target compounds had highest emission rates between 12:00 and 18:00.

Estimated TNMHC emission rates from MH3 are presented in Figure 5.18 and in Table

B.7. Emission rate estimates for TNMHC from MH3 ranged from 3.3 to 168 g/hr.

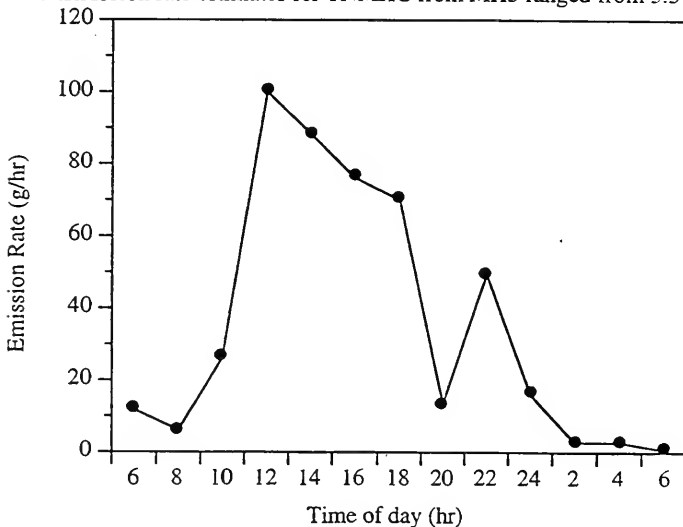


Figure 5.13 MCI Event 4: Toluene Emission Rates from manhole 3.

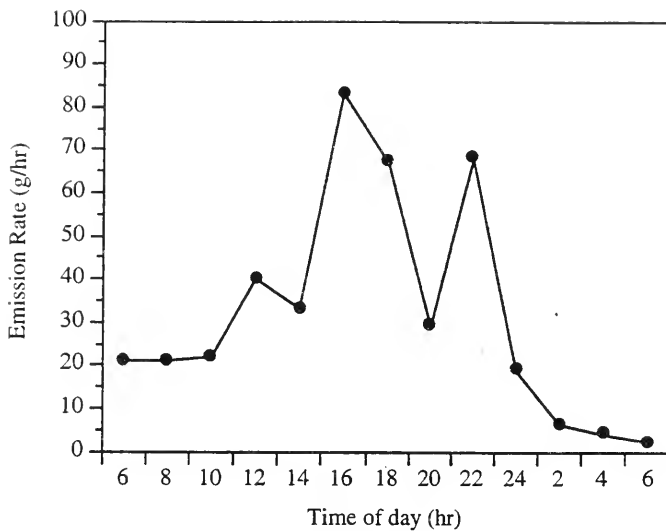


Figure 5.14 MCI Event 4: Total Xylenes Emission Rates from manhole 3.

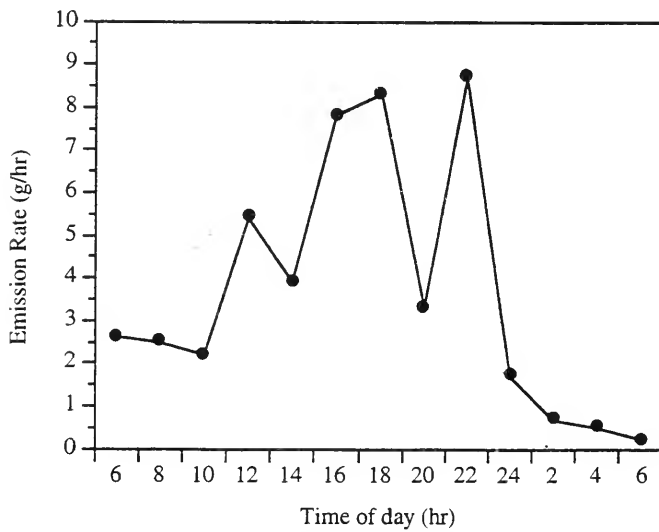


Figure 5.15 MCI Event 4: Ethylbenzene Emission Rates from manhole 3.

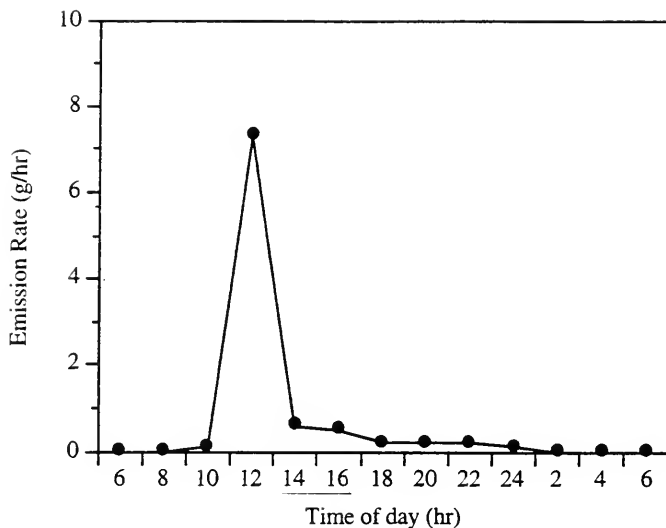


Figure 5.16 MCI Event 4: Tetrachloroethene Emission Rates from manhole 3.

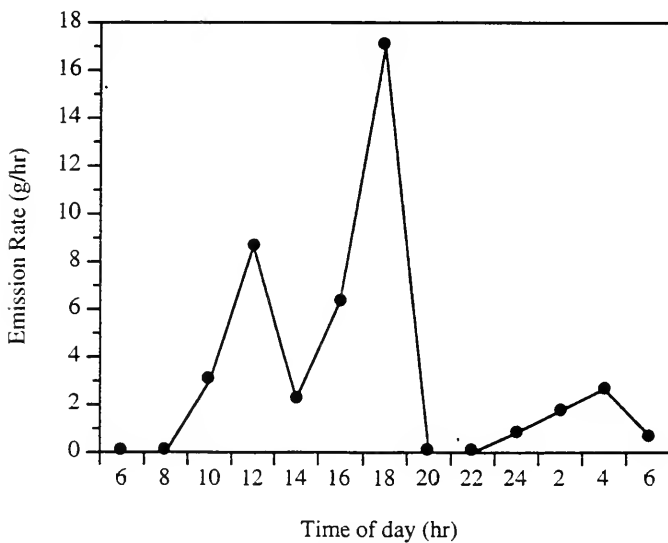


Figure 5.17 MCI Event 4: Benzene Emission Rates from manhole 3.

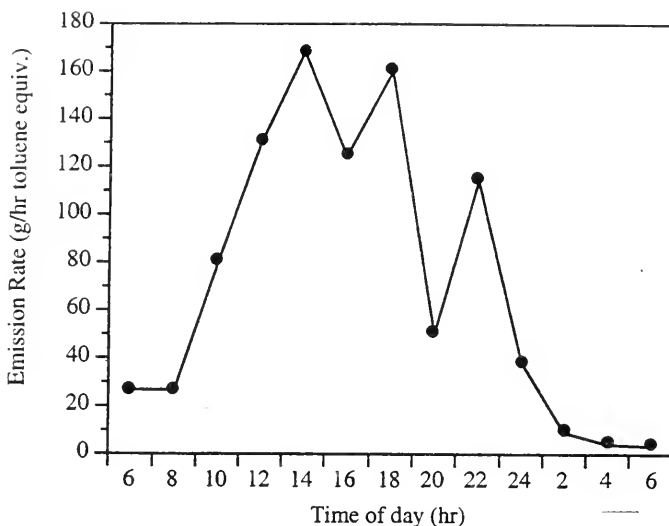


Figure 5.18 MCI Event 4: TNMHC Emission Rates at manhole 3.

Time weighted average system emission rates (TWAER) for target compounds detected during each event are presented in Table 5.1. System emission rates for Event 4 were extrapolated from emissions measured at MH3. Low variation of TNMHC concentrations between the four manholes enabled the use of MH3 target compound concentrations as a system average. System ventilation rates used were extrapolated as previously discussed.

System TWAER were highest for all detected target compounds during Event 4 and lowest during Event 3. Tetrachloroethene was quantified during all four events and had TWAER ranging from 35 to 78 g/day. Benzene, which was only detected during Event 4, had a TWAER of 78 g/day. Toluene had the highest TWAER during Events 1,2 and 4 and ranged from 1800 to 3800 g/day. Ranges of TWAER for ethylbenzene and total xylenes for these three events were 209 to 390 g/day and 67 to 3400 g/day, respectively.

As stated previously, there are several errors associated the measurement of individual manhole ventilation rates and with the collection/analysis of headspace gas samples.

Because of the possibility for these errors there is necessarily an uncertainty associated with the calculation of emission rates utilizing the ventilation rate and headspace concentration. If the assumed error bounds associated with the ventilation rate measurement and determination of compound concentration of $\pm 20\%$ and $\pm 25\%$, respectively, are valid, then it follows that the estimated emission rates are approximately $\pm 50\%$ of the actual values.

5.2 HIGH PARK

5.2.1 Ventilation Rates

Ventilation rates measured during High Park Events 1 to 3 are presented in Figures 5.19 and 5.20, and Tables C.1, C.2, and C.3. Figure 5.19 illustrates the ventilation rate data measured at MH1 located on the Metro Toronto line, while Figure 5.20 shows summed ventilation rates measured from two manholes, MH2 and MH3, located on the City of Toronto line.

Metro Toronto line ventilation rates measured at MH1 (Figure 5.19) ranged from a low of 72 m³/hr at 11:00 of Event 3 to a high of 500 m³/hr at 15:30 of Event 2. Comparison of events at each sampling period revealed that Event 2 ventilation rates were highest during all sampling periods except the 14:00 period. Ventilation rates measured during Events 1, 2 and 3 ranged from 180 to 400 m³/hr, 250 to 500 m³/hr and 72 to 400 m³/hr, respectively. Ventilation rates during Event 1 and 2 generally increased in time from 8:00 to 15:30. Exceptions for Event 1 were measured at 11:00 and 14:00, while the 14:00 measurement during Event 2 was lower than the previous period. Event 3 exhibited the same trends as Event 1 but with different magnitudes.

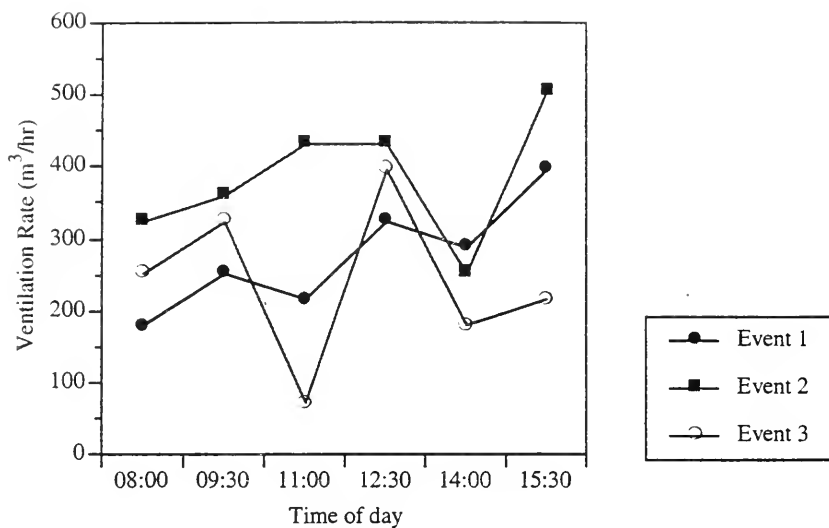


Figure 5.19 HP Events 1 - 3: Ventilation Rates from manhole 1.

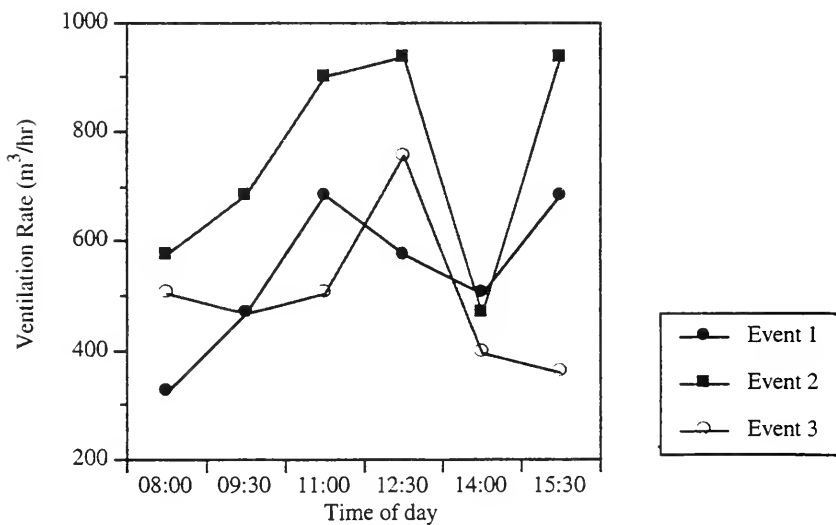


Figure 5.20 HP Events 1 - 3: Combined Ventilation Rates from manholes 2 and 3.

The combined ventilation rates of MH2 and MH3 located along the City of Toronto line are presented in Figure 5.20 and have trends similar to the Metro Toronto line. For all sampling periods except at 14:00, Event 2 was characterized as having the highest ventilation rates. Also, a general trend of increasing rates with time was evident for Events 1 and 2 with the same exceptions discussed above for the Metro Toronto line. System ventilation rates ranged from a low of 320 m³/hr measured at 8:00 during Event 1 to a high of 940 m³/hr for both the 12:30 and 15:30 sampling periods of Event 2. System ventilation rates measured during Events 1, 2 and 3 ranged from 320 to 680 m³/hr, 470 to 940 m³/hr and 360 to 760 m³/hr, respectively.

As stated earlier, additional ventilation rates were measured at two manholes, MH4 and MH5, located downstream of MH3. Measurements at these manholes were taken at 9:30, 12:30 and 2:00 for Event 3. During all three periods, ventilation rates at MH4 were lower than either MH2 or MH3, while MH5 was higher. On average, inclusion of these ventilation rates in the calculation of the system ventilation rates would increase the system rates by approximately 110%.

Time weighted average ventilation rates for both lines are presented in Table 5.2. The Metro Toronto line TWAVR ranged from 6,600 to 9,100 m³/day while TWAVR for the City of Toronto line varied between 12,000 and 18,000 m³/day.

Ventilation rates measured along both lines during Events 1 through 3 at High Park exhibited similar trends. Rates along both lines generally increased with time throughout the day with the exception of Event 3 which had maximum measured rates at 12:30. Both sewers had highest rates during Event 2, the weekend event, and lowest during Event 3, a weekday event. The increase in ventilation rates with time during each event may have

been caused by an increase in wastewater flowrate. However, lack of wastewater flowrate data did not allow the validation of this theory. At present it is not possible to ascertain why the weekend event ventilation data exceeded both weekday events.

Table 5.2 High Park Events 1 - 3 time weighted average ventilation rates, concentrations and emission rates.

	Event 1	Event 2	Event 3
Metro Toronto line (MH1)			
<u>Ventilation Rate</u> (m ³ /day)	6600	9100	5800
<u>Concentration</u> (mg/m ³)			
Toluene	7.5	0.6	7.4
Total Xylenes	18	0.4	8.3
Ethylmethyl Benzene	26	0.2	11
Trimethylbenzene	6.6	-	6.2
Tetrachloroethene	-	0.4	-
Trichloroethene	-	0.6	-
<u>Emissions</u> (g/day)			
Toluene	47	4.8	25
Total Xylenes	103	3.4	42
Ethylmethyl Benzene	170	1.0	58
Trimethylbenzene	43	-	31
Tetrachloroethene	-	3.8	-
Trichloroethene	-	5.3	-
City of Toronto line (MH2 & MH3)			
<u>Ventilation Rate</u> (m ³ /day)	13000	18000	12000
<u>Concentration</u> (mg/m ³)			
Toluene	4.4	0.1	2.0
Total Xylenes	5.2	0.1	2.2
Ethylmethyl Benzene	2.1	0.1	3.8
Trimethylbenzene	4.9	-	1.8
Tetrachloroethene	-	0.2	-
Trichloroethene	-	0.3	-
<u>Emissions</u> (g/day)			
Toluene	54	2.4	21
Total Xylenes	67	1.0	22
Ethylmethyl Benzene	250	1.2	34
Trimethylbenzene	50	-	17
Tetrachloroethene	-	2.6	-
Trichloroethene	-	5.0	-

5.2.2 Headspace Concentrations

Concentrations of both target and non target compounds detected during Events 1 through 3 along the Metro Toronto line (MH1) and the City of Toronto line (MH2 and 3) are presented in Figures 5.21 to 5.23 and 5.24 to 5.26, respectively. Tabulated concentration data for all three events are presented in Tables C.1, C.2 and C.3. Standard curves used in the quantification of target compounds are given in Appendix D.

Toluene and total xylenes were detected along both lines during all three Events. Ethylbenzene was detected in only 13 of 54 samples collected at MH1 through MH3, and exceeded 1 mg/m^3 only five times. Two additional target compounds; tetrachloroethene (PERC) and trichloroethene (TCE) were detected during Event 2 along both lines. Two nontarget compounds were detected during most sampling periods along both lines and were identified as isomers of the ethylmethyl benzene (EMB) and trimethylbenzene (TMB) groups. Although standards for these compounds were unavailable, their quantification was expressed in xylene equivalents.

During Event 1, the highest concentrations measured for all detected compounds at MH1 (Figure 5.23) was recorded at 9:30. Minimum concentrations for total xylenes, EMB and TMB occurred at 15:30 while toluene was lowest at 14:00. Concentration ranges measured during Event 1 were: toluene (0 to 24 mg/m^3), total xylenes (0.7 to 63 mg/m^3), EMB (2.9 to 56 mg/m^3), and TMB (0.2 to 15 mg/m^3).

Concentrations of compounds detected at MH1 during Event 2 are given in Figure 5.22. Although toluene, xylenes, EMB, PERC and TCE were detected, only toluene ever exceeded one mg/m^3 .

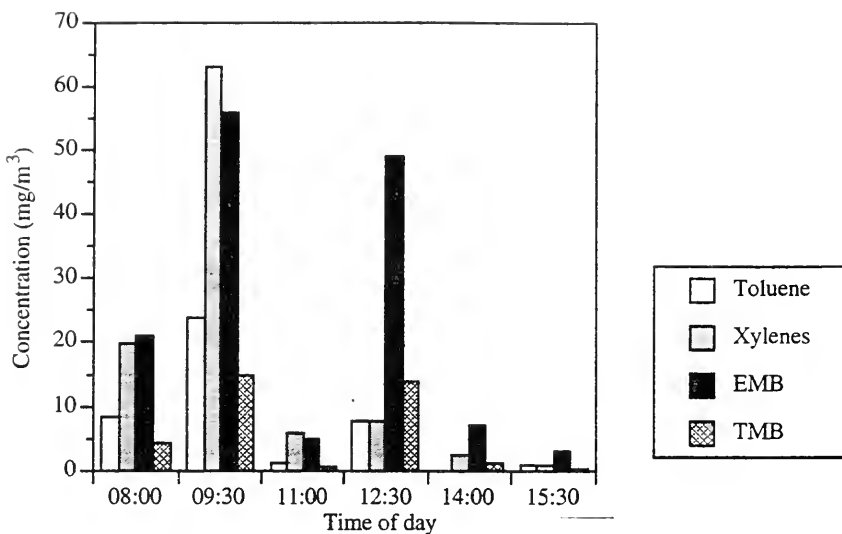


Figure 5.21 HP Event 1: Compound Concentrations at manhole 1.

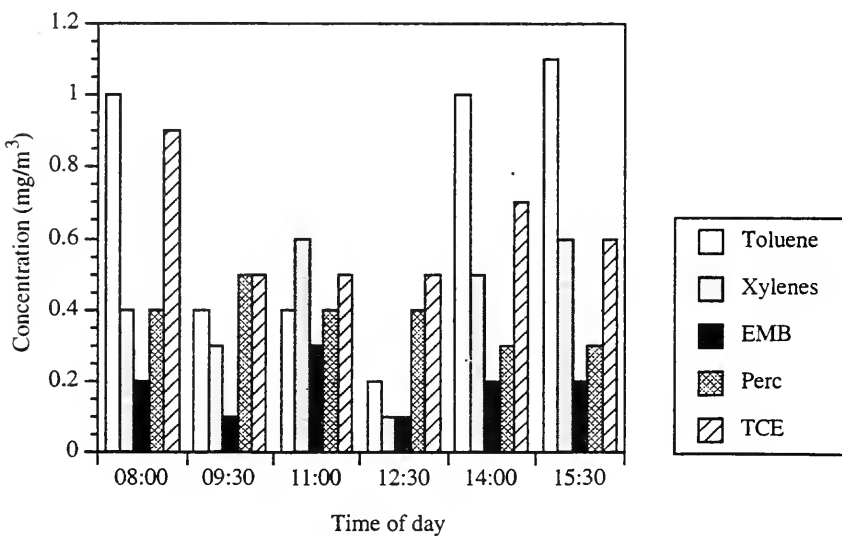


Figure 5.22 HP Event 2: Compound Concentrations at manhole 1.

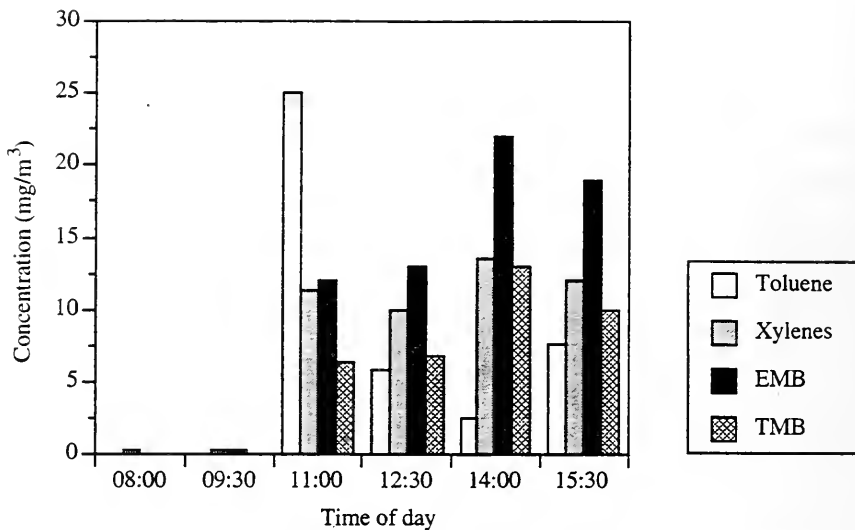


Figure 5.23 HP Event 3: Compound Concentrations at manhole 1.

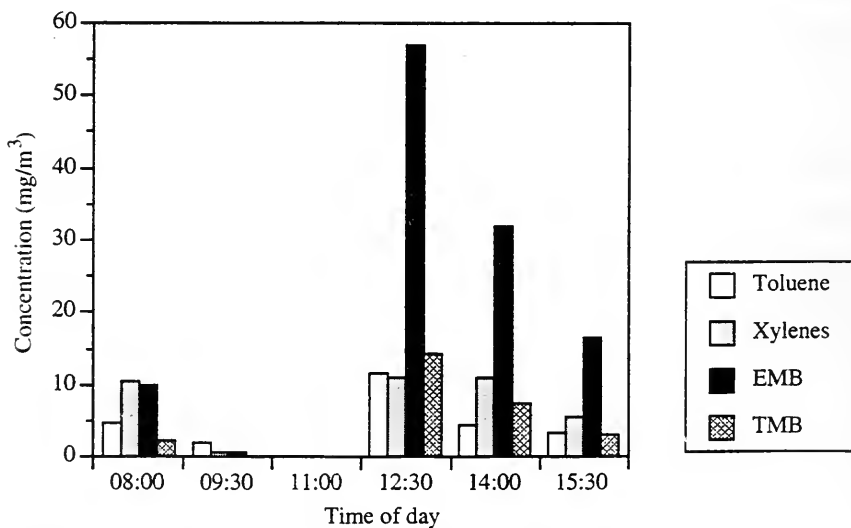


Figure 5.24 HP Event 1: Average Compound Concentrations at manholes 2 and 3.

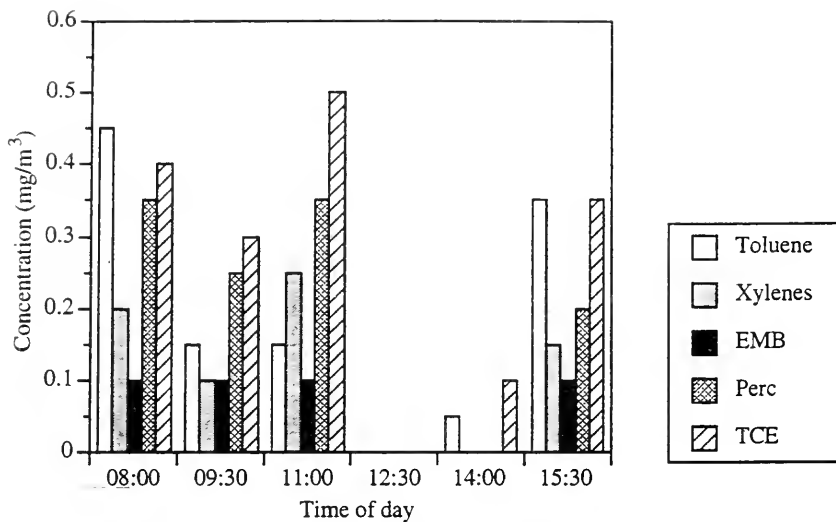


Figure 5.25 HP Event 2: Average Compound Concentrations at manholes 2 and 3.

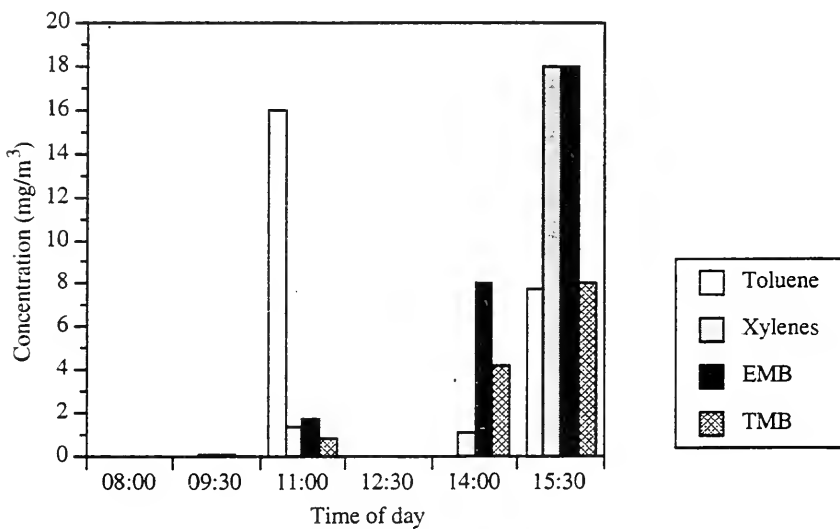


Figure 5.26 HP Event 3: Average Compound Concentrations at manholes 2 and 3.

Compound concentrations measured at MH1 during Event 3 are presented in Figure 5.23. Minimum concentrations for all quantified compounds occurred at 8:00. Highest concentrations for the xylenes, EMB and TMB were observed at 14:00, while toluene peaked at 11:00. Concentration ranges measured during Event 1 were: toluene (0 to 25 mg/m³), total xylenes (0.3 to 14 mg/m³), EMB (0.1 to 22 mg/m³), and TMB (0 to 13 mg/m³).

Concentrations measured along the City of Toronto line at MH2 and MH3 are similarly presented in Figures 5.24 to 5.26.

Minimum and maximum average concentrations for all quantified compounds occurred at 11:00 and 12:30, respectively, in Event 1 (Figure 5.26). Both toluene and total xylenes ranged between 0 and 11 mg/m³. Ranges for EMB and TMB were 0 to 57 mg/m³ and 0 to 15 mg/m³, respectively.

Similar to the Metro Toronto line during Event 2, low concentrations were detected along the City of Toronto line. As shown in Figure 5.25, average concentration never exceeded 0.5 mg/m³.

Maximum average concentrations measured along the City of Toronto line during Event 3 for total xylenes, EMB and TMB occurred at 15:30 (Figure 5.26), while toluene was highest at 11:00. The four compounds were not detected at either 8:00 or 12:30. Maximum concentration measured for each compound varied from 8 to 18 mg/m³.

Headspace samples were also collected at MH4 and MH5 at 9:30, 12:30 and 14:00 during Event 3. No compounds were detected during the 9:30 sampling period. Toluene,

xylenes, EMB and TMB were all detected at 12:30 and 14:00 at both manholes and were of the same order of magnitude as those measured elsewhere during Event 3.

Time weighted average concentrations are presented in Table 5.2 for each event and sewer line. During Event 2, TWAC were below 1 mg/m^3 for all compounds. During Events 1 and 3 and for both sewer lines, toluene TWAC fell between 2.0 and 7.5 mg/m^3 while total xylenes varied between 2.2 and 18 mg/m^3 . Values of TWAC for the nontarget compound, ranged from 2.1 to 26 mg/m^3 for EMB, and 1.8 and 6.6 mg/m^3 for TMB.

As was observed for the MCI, headspace concentrations were highly variable along both lines during the weekday events. Concentrations were very low during the weekend event (Event 2).

Concentration profiles for the four compounds detected during Events 1 and 3 along both lines were very similar suggesting that each line received these compounds from one source. It is also interesting to note that, for all three events, each sewer contained the same compounds, although present at different times. It is possible that either one or several identical sources discharged VOCs into both sewers.

During Event 3, samples at MH4 and MH5 contained detectable quantities of several compounds which, during the same sampling period, were not detected upstream at either MH2 or MH3. One explanation for these occurrences is the time lag associated with sampling. Samples were collected at MH4 and MH5 approximately 15 minutes after MH3. Because of this time interval, if the sewer headspace air traversed the sewer in a plug-like fashion, it may have been possible that the samples taken at MH4 and MH5 represented different headspace volumes than sampled upstream at MH2 and MH3.

5.2.3 Emission Rate Estimates

Emission rates for Events 1 and 3 for both sewer reaches are presented in Figures 5.27 to 5.30. Tabulated emission rates for all three events are also presented in Tables C.1, C.2 and C.3. Emission rates from the Metro Toronto line were obtained from data collected at MH1, while emission rates from the City of Toronto line were estimated by summing emissions from MH2 and MH3. During all Event 2 sampling periods, and at all locations, all compounds quantified had emission rates lower than 0.6 g/hr.

Emission rate estimates for the Metro Toronto line during Event 1 are presented in Figure 5.27. Toluene and xylenes were emitted in highest amounts at 9:30, while the highest rates for EMB and TMB were detected at 12:30. Emission rates for toluene and xylenes ranged from 0 to 5.8 g/hr and 0.3 to 15 g/hr, respectively. Emission rates of EMB varied between 1.1 and 16 g/hr while TMB ranged from 0 and 4.7 g/hr.

Emission rates measured during Event 1 along the City line are depicted in Figure 5.28. The same compounds as detected along the Metro line were observed along the City line. However, while the Metro line generally had highest emission rates of compounds generally in the morning, and falling off after 12:30, the City line did not appear to have significant emissions until the 12:30 sampling period. Emissions were highest for all four compounds at 12:30 and lowest at 11:00. Emissions of toluene, xylenes and TMB ranged from 0 to approximately 6.4 g/hr while EMB emissions peaked at 33 g/hr (xylene equivalents).

Event 3 emission estimates from MH1 are presented in Figure 5.29. Low emission rates were observed during the first two sampling periods. Emission rates were again highest during the 12:30 sampling period and then tailed off with time for the xylenes, EMB and

TMB. The lowest emission estimates for all compounds were less than 0.2 g/hr and occurred during the 8:00 sampling period. In terms of emission rates, the compounds in descending magnitude were: EMB (5.1 g/hr), xylenes (4.2 g/hr), TMB (2.7 g/hr), and Toluene (2.4 g/hr).

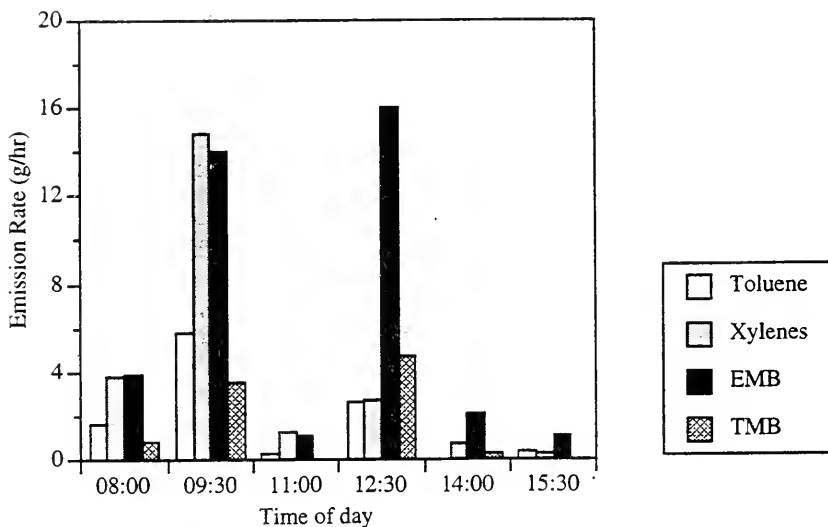


Figure 5.27 HP Event 1: Emission Rates from manhole 1.

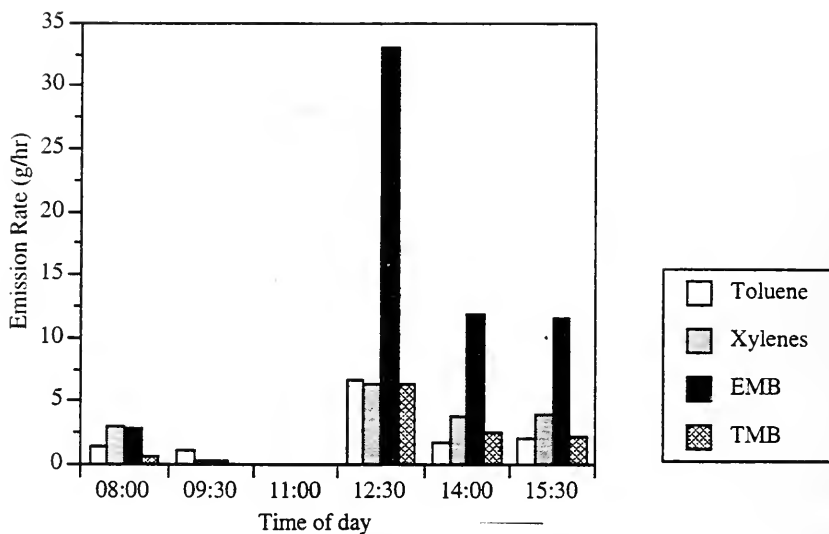


Figure 5.28 HP Event 1: Combined Emission Rates from manholes 2 and 3.

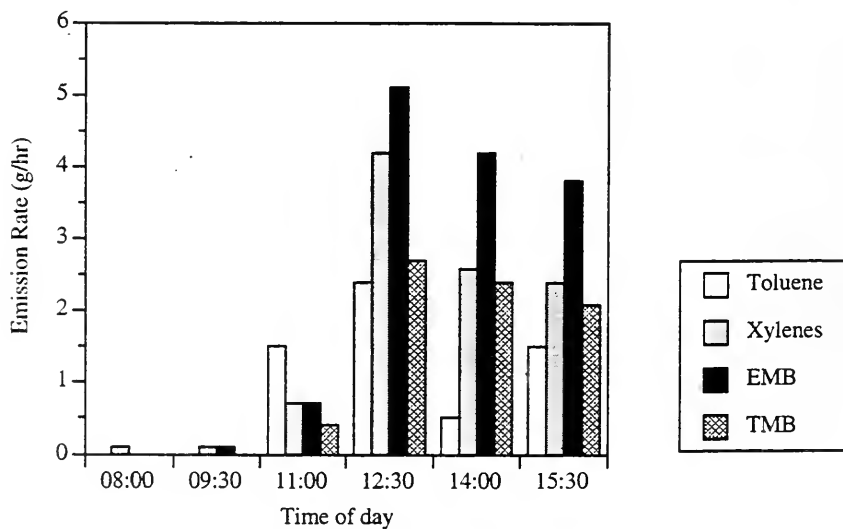


Figure 5.29 HP Event 3: Emission Rates from manhole 1.

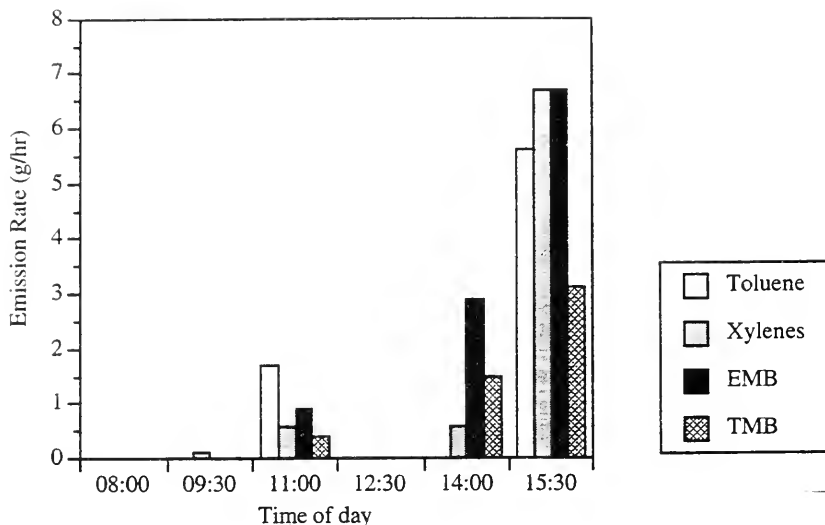


Figure 5.30 HP Event 3: Combined Emission Rates from manholes 2 and 3.

Emission rates during Event 3 are illustrated in Figure 5.30 for the City of Toronto reach. Emission rates were low during the first four sampling periods. Only toluene, during the 11:00 period, exceeded 1 g/hr. Emissions were highest for all four compounds at 15:30. Xylenes and EMB had rates of 6.7 g/hr followed by toluene at 5.6 g/hr and TMB at 3.1 g/hr.

As expected, due to the increased system ventilation rates and the presence of compounds in samples collected at MH4 and MH5, inclusion of these manholes in the estimation of emission rates from the City of Toronto line would greatly increase the estimated rates. For example, the estimated emission rate for toluene at 12:30 of Event 3 based on MH2 and MH3 was 0 g/hr. Including emissions of toluene measured at MH4 and MH5 would result in a total system estimate of 5.5 g/hr.

Time weighted average emission rates for both sewer lines and all three events are presented in Table 5.2. During Event 2, all compounds had TWAER less than 6 g/day along both lines.

Toluene TWAER during Events 1 and 3 for both lines ranged between 21 and 54 g/day while TWAER for total xylenes varied between 22 and 103 g/day. Similarly, the nontarget compounds EMB and TMB had TWAER ranges of 34 to 250 g/day and 17 to 50 g/day (xylene equivalents).

It should be noted that emission estimates for the Metro Toronto line were based on data from one manhole only and that in all likelihood there are additional manholes located along this line from which emissions occur. Similarly, emissions for the City of Toronto line were estimated using only MH2 and MH3. Sampling at MH4 and MH5 indicated that significant emissions occurred at those two locations. Therefore, inclusion of MH4 and MH5 would have substantially increased total emissions of VOCs from this sewer.

Potential sources of error regarding the ventilation rate measurement, headspace concentration quantification and compound emission rate estimation for the High Park site are the same as those described earlier for the MCI. It is expected that individual manhole ventilation rates, headspace concentrations and estimated emission rates are approximately $\pm 20\%$, $\pm 25\%$, and $\pm 50\%$, respectively, with respect to actual values.

5.3 SOURCE COMPARISON OF VOC EMISSIONS

To ascertain the relative importance of VOC emissions from WCSs, a comparison between the estimated emission rates obtained during the MCI and High Park Site monitoring events and previously reported emissions from four WWTFs was performed. Because of the

proximity of the two WCSs at High Park an area source emission rate, obtained by summing emissions from both sewers, was used. The comparison was limited to target compounds detected during field monitoring.

The four WWTFs were located in southern Ontario and were, in order of increasing industrial flow contribution: Waterloo, Highland Creek, Burlington-Skyway and Lakeview. Bell *et al.* (1988) monitored each plant for four consecutive weekdays and reported average emission rates. Monitoring at each plant was performed at both aerated grit chambers and activated sludge reactors which were believed to be the sites at which the majority of stripping occurred. Emission rate estimates were obtained by summing emissions from both processes. Plant monitoring was performed only during weekdays. Therefore, emission estimates for the two sites utilized in the comparison were limited to weekday events. Since all but one field monitoring were limited to 7.5 to 8 hour intervals, data obtained during the diurnal event were used to develop a correction factor needed to extrapolate between shorter monitoring periods and a 24 hour period. This factor was obtained by comparing TWAER for the 8:00 to 16:00 period of the diurnal event with the diurnal TWAER. The factor used to convert all events into 24 hour TWAER was 0.7, and although obtained from MCI data, was used for both the MCI and High Park sites.

Results of this comparison are provided in Table 5.3. Emissions of toluene, ethylbenzene and total xylenes from the MCI were greater than for all plants monitored. In addition, emissions of tetrachloroethene from the MCI were similar in magnitude to all plants except Lakeview. Emission rates from the High Park area were much lower than either the MCI or all plants except the Waterloo facility. However, emission rates for the High Park area were based on emissions from manholes 1 through 3. It is expected that inclusion of manholes 4 and 5 in the emission rates would significantly increase the total emission rates from the High Park area.

Table 5.3 Source comparison of VOC emissions.

Source	Emissions (g/day)			
	Ethylbenz.	Toluene	Xylenes	PERC
MCI ¹	230	2300	1400	47
High Park Area ²	-	52	82	-
Burlington-Skyway ³	29	520	130	48
Highland Creek ⁴	30	270	220	61
Lakeview ⁵	92	360	410	160
Waterloo ⁶	< 1	2.1	< 1	17

1: 0.18 m³/s average flowrate.

2: unknown average flowrate.

3: 0.88 m³/s average flowrate.

4: 0.91 m³/s average flowrate.

5: 0.74 m³/s average flowrate.

6: 0.34 m³/s average flowrate.

In general, emission rates from both High Park sewers were much lower than from the MCI. However, mass loadings to each line would have to be known in order to perform a comparison on a relative basis.

It should also be evident from the results of this comparison that emission rates from wastewater treatment plants are highly variable. Individual treatment plant emission rates depend on many factors including compound mass loading rates, what processes/units are present and actual plant operating conditions.

The results presented in Table 5.3 are not intended to serve either as a definitive comparison between all sewers and wastewater treatment plants or as a means of predicting the absolute emission rates from sewers. The intention of this comparison is to draw

attention to the potential for significant emission rates from some sewers believed to represent worst case scenarios.

The results tabulated in Table 5.3 suggest that emissions of some VOCs may be significant prior to wastewater treatment, and that total emissions from some sewers may be much larger than those from downstream treatment facilities. It is possible that a large fraction of VOCs discharged to WCSs are emitted to the atmosphere during conveyance, and that VOC mass loadings at WWTF are small relative to amounts originally discharged.

As stated earlier, there is an expected error bound of $\pm 50\%$ with respect to the estimated emission rates. However, even if it were assumed that the estimates overpredicted the emission rates by a factor of two, the revised emission rates for the MCI would still exceed all other sources in Table 5.3 for all compounds except tetrachloroethene (PERC).

The relative amounts of stripping which occur at hydraulic drop structures and along uniform sections of sewer reach were examined by measurement of wastewater VOC concentrations at these locations. An assumption that all losses of VOC from wastewater were attributable to stripping enabled a direct correlation between VOC losses from wastewater and stripping efficiency. This assumption should be valid for drop structures and short reaches of sewer.

6.1 SYSTEM DESCRIPTION

Stripping of VOCs along a sewer reach was studied using the MCI. A schematic of the MCI is presented in Figure 4.1. In order to determine the relative importance of VOC stripping at hydraulic drop structures versus stripping along uniform sections of reach, the section of the MCI bounded by MH9 and MH3 was studied. This section of reach contained two drops, located at MH8 and MH7, and a uniform section between MH6 and MH3 (Figure 6.1).

6.2 EXPERIMENTAL EVENTS

Two liquid sampling events were completed. Event 5, performed on Thursday May 27, 1993, involved liquid and gas sampling along the MCI at various locations over a two hour interval. Event 6 was completed on Wednesday November 10, 1993 and involved liquid sampling along the MCI over a one hour interval.

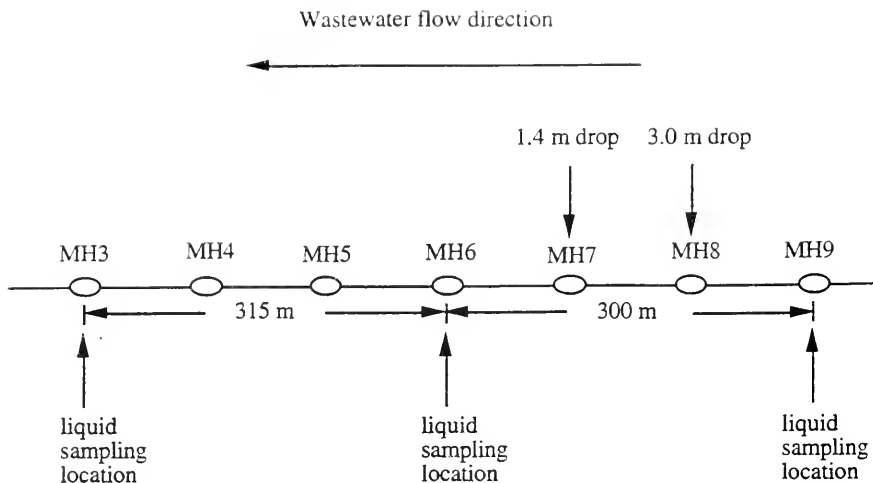


Figure 6.1 Liquid sampling locations along the MCI.

Sample collection during Event 5 was performed between 14:00 and 16:00 hours. Wastewater grab samples were collected at three locations along the MCI: MH9, MH6 and MH3 (see Figure 6.1). Starting at 14:00 hours a total of 11 samples, one taken approximately every ten minutes, were collected at MH9. A total of 11 wastewater samples at MH6 were similarly collected covering 105 minutes. A total of eight wastewater samples were collected at MH3 spanning 105 minutes. Eight gas samples were also collected during Event 5. Two samples were collected per location, at MH7, MH6, MH5 and MH3. Wastewater flow rates were continuously monitored at MH3 and recorded approximately every 20 minutes.

Wastewater samples were collected between 13:30 and 14:30 during Event 6. A total of seven samples were collected at MH9, one taken approximately every ten minutes. Four samples were obtained at MH6 over this same time period. Wastewater flow rates were continuously monitored at MH3 and recorded approximately every 20 minutes.

6.3 SAMPLING METHODOLOGIES

Outgassing Flow Rate Measurements. Flow rate measurements were obtained by anemometer using the same method described for the emissions monitoring events. In addition to the measurement of ventilation rates by anemometer during Event 5, system ventilation rates were quantified by dilution of sulfur hexafluoride (SF₆) gas. Measurement of the ventilation rate using SF₆ was accomplished by injecting a known concentration at a known volumetric flowrate into the MCI headspace at MH9, and then collecting outgassing air samples at MH8 using plastic 5 mL airtight syringes. Outgassing air samples were collected approximately every ten minutes with individual sample collection time lasting approximately 15 seconds. The concentration of SF₆ in the collected samples was quantified using GC/ECD. Ventilation rates were then determined by mass closure analysis assuming no losses.

Sewer Headspace Sampling. Headspace samples were collected during Event 5 using the same method described for the emissions monitoring events.

Wastewater Sample Collection. Wastewater grab samples were drawn from the MCI to ground level through weighted, submerged 6 mm o.d. Teflon tubing. Continuous wastewater pumping was performed by peristaltic pumps driven by portable gas generators. Grab samples were collected in 40 mL EPA certified glass vials. Each sample was filled to capacity ensuring zero headspace and then sealed with teflon lined screw caps. Wastewater samples were stored in an ice chest while in the field. Once returned to the laboratory, all samples were refrigerated at 4 ° C prior to analysis.

Wastewater Flowrate Measurement. Wastewater flowrate measurements were obtained through the use of an existing flowmeter stationed at MH3 and was recorded approximately every 20 minutes.

6.4 SAMPLE ANALYSIS

Gas samples collected during Event 5 were analyzed as previously described. Analysis of liquid samples required that the samples were first loaded onto adsorbent tubes. Liquid samples were injected into a 10 mL sparging vessel prior to concentration on a Carbotrap 300 adsorbent tube connected to the vessel. The sample was purged at 100 mL/min for 10 minutes using charcoal-polished ultra-high purity (UHP) nitrogen. Previous analyses indicated that a purge volume of one liter was sufficient to remove all volatile tracers from solution without causing mass breakthrough. However, previous studies regarding purge volumes were performed using potable water and not wastewater. It is possible that any solids contained in wastewater samples may have sorbed a significant fraction of the total amount of chemical present in the sample. If this is the case, then it is important that sufficient time be allowed during purging to ensure that chemical desorption from the solids occurs. Therefore, it is suggested that prior to further wastewater sample preparation using this protocol, similar testing be performed using wastewater to ensure the validity of both the purge volume flowrate and purging time.

Samples collected during Event 6 were analyzed at the Wastewater Technology Centre in Burlington, Ontario. Liquid samples collected at MH9 and MH6 were composited prior to analysis resulting in one composite sample per manhole.

7.1 MCI EVENT 5

Wastewater flowrates measured at MH3 and headspace ventilation rates measured using SF₆ during Event 5 are presented in Figure 7.1. Wastewater flowrates were very consistent over the two hour interval and averaged 0.20 m³/s. System ventilation rates measured over the 80 minute SF₆ sampling period ranged between 0.31 and 0.55 m³/s and averaged 0.43 m³/s. The $Q_{\text{air}}/Q_{\text{ww}}$ and $v_{\text{air}}/v_{\text{ww}}$ ratios for this event were 2.2 and 0.4, respectively, which are very similar to values obtained during the emissions monitoring events in which historical wastewater flowrate data and anemometer derived system ventilation rates were used. It is important to note that while these ratios may be appropriate for estimating average ventilation rates for systems over a time interval of hours, use of such a ratio might not work for short time intervals over which rapid fluctuation of ventilation rates might occur. This is demonstrated in Figure 7.1 in which the instantaneous ventilation rates do not appear to have any correlation to wastewater flow. One explanation for this observation is that instantaneous fluctuations or deviations from the average ventilation rate may be caused by transient factors such as rapid changes in horizontal wind speeds moving across the manhole covers. Such changes may serve to cause temporary movement of air into or out of manholes but may, in themselves, not be capable of generating sustained sewer ventilation.

System ventilation rates for the time period 15:00 to 16:00 were also estimated using the anemometer method described previously and are presented in Table E1. This method resulted in a system ventilation rate of 0.36 m³/s which is lower than, but comparable to, the SF₆ based estimate. The difference could be attributable to the fact that an estimation of

system ventilation rates using the anemometer technique requires that all outgassing sites be quantified. Failure to measure all outgassing sites may have resulted in an underprediction of system ventilation rates. During the preliminary site visit outgassing at manhole 1 was observed. It is possible that inclusion of this manhole in estimating system ventilation rates using hot wire anemometry would result in rates closer in magnitude to the rates measured using SF₆. Another explanation for the difference is that there is a potential $\pm 15\%$ error associated with GC/ECD analysis of the SF₆ samples which would result in estimated system ventilation rates that are $\pm 15\%$ of the actual value.

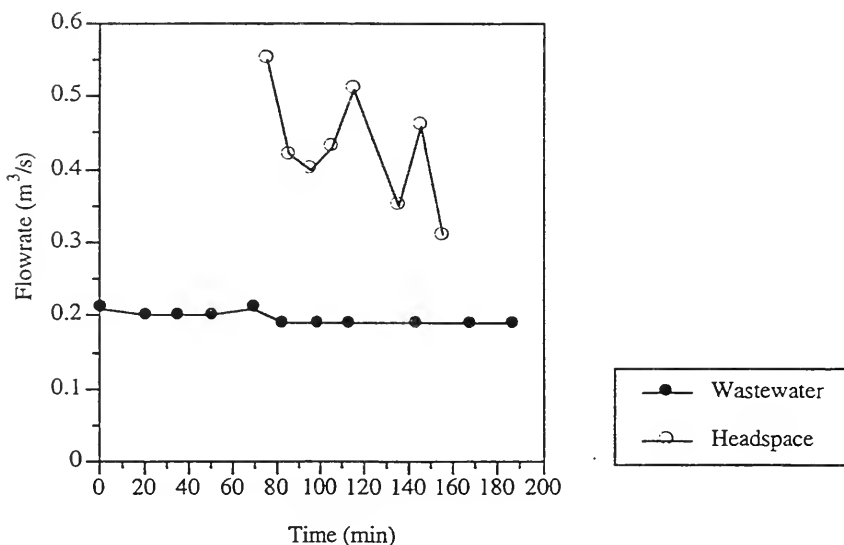


Figure 7.1 Event 5 Wastewater and Headspace Ventilation Flowrates.

Analysis of wastewater samples collected during Event 5 indicated high concentrations of toluene, ethylbenzene, m,p-xylene and o-xylene. Quantification of toluene was not possible as the predicted masses determined during GC/MS were in excess of the highest standard. Visual inspection of collected wastewater samples indicated that a solvent free

phase was not present. Based on this observation it was possible to predict an upper range for the toluene concentration due to solubility limitations. Assuming that the solubility of toluene in wastewater is comparable to potable water and that the wastewater temperature was approximately 20 °C, the upper range for possible toluene concentration should be approximately 500 mg/L (MacKay *et al.* 1992.) Toluene concentrations for all samples were therefore estimated to be in excess of 10 mg/L but less than 500 mg/L. Concentrations of ethylbenzene, m,p - xylene and o - xylene measured during Event 5 at MH9, MH6 and MH3 are presented in Figures 7.2, 7.3 and 7.4 and listed in tabular form in Table E.2. It is apparent from these figures that there was high temporal variability in compound concentrations, with all compounds having minimum and maximum detected concentrations differing by at least a factor of two at all three sampling locations. As expected, compound concentrations were generally highest at MH9, lowest at MH3 and decreased in the direction of wastewater flow. Slight shifting of peaks between MH9, MH6 and MH3 was observed and can be attributed to the wastewater transit time between sampling locations. Based on information regarding sewer lengths between sampling locations and average wastewater velocity, it was estimated that time lags of approximately four minutes were present between MH9 and MH6, and MH6 and MH3.

Concentrations of all three compounds measured at MH9 are presented in Figure 7.5. The similarity in trends with respect to temporal variations for the three compounds suggests that the presence of these compounds are linked. One possible explanation is that these compounds originate from the same source.

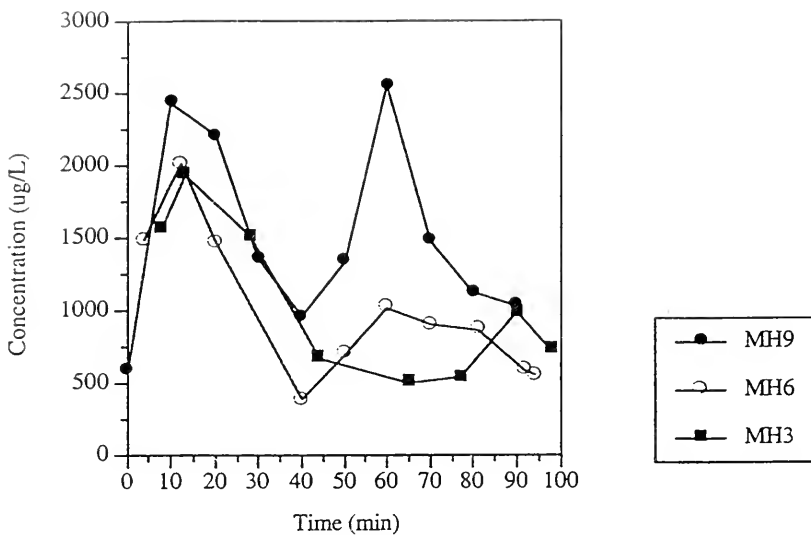


Figure 7.2 Event 5 Ethylbenzene Wastewater Concentrations at manholes 9, 6, and 3.

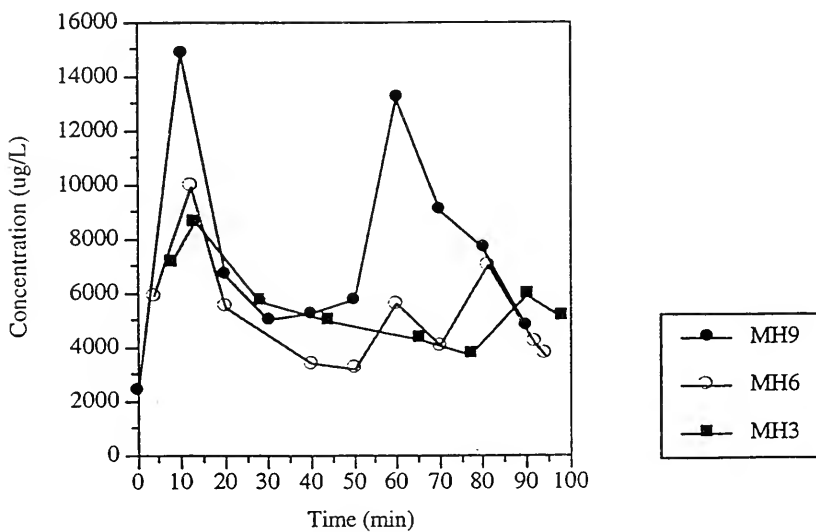


Figure 7.3 Event 5 m,p-Xylene Wastewater Concentrations at manholes 9, 6, and 3.

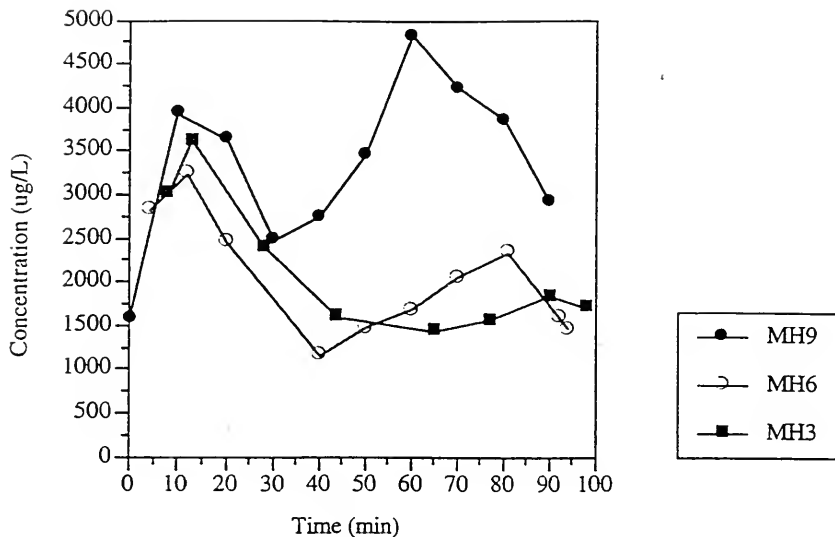


Figure 7.4 Event 5 o-Xylene Wastewater Concentrations at manholes 9, 6, and 3.

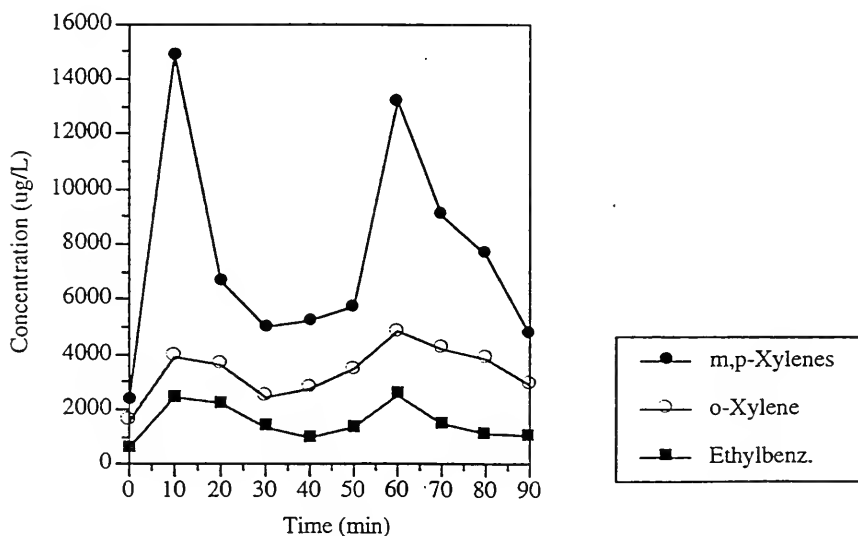


Figure 7.5 Event 5 Compound Wastewater Concentrations at manhole 9.

Because the wastewater flowrate was relatively constant over the sampling time period TWACs could be used to predict stripping efficiencies across the drop structures and the uniform section of reach. Average compound concentrations at all three sampling locations are presented in Table 7.1. In order to account for the time lag associated with wastewater transit between locations, the following time periods were utilized for the averaging process: MH9, 0 - 90 min; MH6, 4 - 94 min; and MH3, 8 - 98 min. If samples were not collected at the specific times desired then concentrations were estimated by interpolation. Comparison of the measured percent stripped across the drop structures with percent stripped along the uniform reach indicates that stripping at the drop structures dominated stripping along the uniform reach. The percent stripped measured across the two drop structures for the three compounds ranged from 34 to 43% while the percent stripped measured along the uniform reach bounded by MH6 and MH3 did not exceed 1.0%.

Table 7.1 Massey Creek Event 5: Percent Stripping Results

Compound	Ave Liq. Concentration (µg/L)			Measured Percent Stripped	
	MH9	MH6	MH3	MH9 - MH6	MH6 - MH3
Ethylbenzene	1600	980	970	39	1.0
m,p-Xylene	7900	5200	5400	34	-3.8
o-Xylene	3500	2000	2000	43	0

The values presented in in Table 7.1 are not intended to be definitive stripping efficiency estimates. This study was performed in order to obtain "ball park" estimates and to also compare on a relative basis, the stripping across drops versus stripping along a uniform section of reach.

Gas samples and ventilation rates based on hot wire anemometry were obtained during Event 5 in the same manner as during previous emissions monitoring events. Compound concentrations, ventilation rates and emission rate estimates are presented in Table E.1. Based on these data, system emission rates for ethylbenzene, m,p-xylene and o-xylene were 17, 95 and 19 g/hr, respectively. Emission rate estimates based on stripping efficiency values, liquid concentrations and wastewater flowrate for ethylbenzene, m,p-xylene and o-xylene were 450, 1900 and 1000 g/hr, respectively. One reason for this large difference could be the fact that the average emission rate based on headspace sampling was obtained from only two samples per location over the entire sampling period. It is possible that large temporal variations in headspace concentration occurred and that periods of high concentration were not sampled. Another explanation is that not all sites emitting VOCs were sampled. Individual emission rate estimates based on anemometry and headspace concentration data are also susceptible to error. Emission rates predicted using the wastewater concentrations, wastewater flowrate and estimated stripping removal efficiencies are also prone to several potential sources of error. Determination of TWACs relied upon the averaging of concentrations determined for several instantaneous grab samples obtained at various times over the entire event. It is possible that the limited number of samples taken during the event were not sufficient in obtaining a true average concentration. Secondly, preparation and analysis of each wastewater sample could also lead to errors. Preparation of each sample for analysis relied on a purge and trap method not previously tested for use with wastewater. Quantification errors associated with GC/MS analysis of each sample is also possible.

One manner in which some uncertainty might be reduced is through the use of Tedlar bags for wastewater sample collection. Instead of obtaining several grab samples and then averaging individual concentrations, the use of Tedlar bags would allow for continuous wastewater sampling. In addition, it is possible to fill these bags in a manner such that

there is no headspace present eliminating any potential losses due to volatilization during the event. It is expected that using the Tedlar bag would result in a more accurate average concentration. Uncertainty could be even further reduced in obtaining TWAC values if it were possible to inject VOCs at a known mass flowrate into the sewer upstream of the section studied. Use of a VOC cocktail containing unique or traceable VOCs would add some control not present during Events 5 or 6. As can be seen from Figure 7.5 there is substantial variation of "in house" VOC concentrations. This variation could be eliminated by the use of a VOC cocktail.

Gas and liquid concentrations can be related at equilibrium using Henry's law. Therefore, if gas and liquid concentrations and wastewater temperature are known, it is possible to determine how close the headspace gas is to being in equilibrium with the wastewater. Wastewater temperatures were not recorded during Event 5 or 6. However, both ambient and sewer headspace gas temperatures were recorded during the diurnal event. Early in the morning (6:00), the sewer headspace gas temperature was 17 °C while the ambient temperature was 14 °C indicating that ambient air entering the system was being heated by the wastewater. Later in the day (14:00), the ambient temperature had increased to 24 °C while the headspace temperature had increased to only 21 °C indicating that at this time the wastewater was cooling the ingassing ambient air. Assuming that the wastewater temperature was constant over this time interval it is possible to predict a plausible wastewater temperature range of between 17 and 21 °C. However, as the diurnal event was performed in July and the liquid sampling events were performed in late May and early November it is expected that the wastewater temperature during these events would be somewhat lower. Therefore to account for this difference a wastewater temperature range of 15 to 20 °C was used in all studies. Results of this study comparing average gas concentrations with MH6 wastewater average concentrations are presented in Table 7.2. The degree of saturation term (DoS) refers to how close the headspace is to equilibrium

with respect to the wastewater. At DoS equal to 100%, gas and wastewater are in equilibrium. For all three compounds and both temperatures, DoS did not exceed 6% indicating relatively low compound gas phase accumulation. One means of maintaining a low gas phase concentration is through the frequent exchange of the sewer headspace air. Based on the finding regarding DoS, therefore, it is possible to model the MCI as a well ventilated system.

Table 7.2. Event 5: Headspace Gas Degree of Saturation

Compound	C _{gas} ave (µg/L)	C _{liq} ave (µg/L)	Hc (15 °C)	C _{gas} equil. (µg/L)	DoS ¹ (%)
Ethylbenz.	12	980	0.19	186	6
m,p-xyl.	70	5200	0.21	1092	6
o-xylene	14	2000	0.15	300	5
Compound	C _{gas} ave (µg/L)	C _{liq} ave (µg/L)	Hc (20 °C)	C _{gas} equil. (µg/L)	DoS ¹ (%)
Ethylbenz.	12	980	0.25	245	5
m,p-xyl.	70	5200	0.25	1300	5
o-xylene	14	2000	0.18	360	4

1. DoS refers to the degree of saturation of the headspace. (DoS = C_{gas} ave/C_{gas} equil)

7.2 MCI EVENT 6

During Event 6 a total of five wastewater flowrates were measured ranging from 0.19 to 0.20 m³/s. The average wastewater flowrate during the sampling period was 0.19 m³/s. As described earlier, seven wastewater samples were collected at MH9 and four wastewater samples were collected at MH6 over the one hour sampling period. Prior to analysis,

samples were mixed together resulting in one composite sample per sampling location. Sample analysis results are presented in Table E.3. In addition to toluene, m,p-xylenes, o-xylene and ethylbenzene, another 8 compounds were identified and quantified. Concentrations of the compounds quantified during both events were approximately one order of magnitude less in Event 6 than Event 5. Possible explanations for this disparity are compound mass flow discharges rate were lower during Event 6 than in Event 5, and the fewer number of grab samples taken during Event 6 did not accurately represent average concentrations.

7.3 MODEL ASSESSMENT

Based on the findings of the study concerning the degree of saturation of the headspace in Event 5, it was possible to approximate the quantity ($C_{liq} - C_g/H_c$) by knowledge of C_{liq} . This allowed use of Equation 15, derived previously in Chapter 3, to predict stripping across the two drop structures located at manhole 8 and manhole 7.

In order to predict the total percent stripped across the two drops it was necessary to first calculate r_0 estimates for each drop. Individual r_0 for each drop were then multiplied together to obtain a total r_0 estimate over the two drops. System parameters used in the calculations are presented in Table 7.3. To facilitate use of the equations developed by Nakasone (1986) it was necessary to estimate values for H, q and T. The value of H and T were assumed to be the same as the depth of flow measured at MH3. Calculation of q required an estimation of weir width (W). This was accomplished through simple geometry knowing the sewer radius and depth of flow. Weir widths used were equal to calculated wastewater surface widths. Two wastewater temperatures were evaluated, 15 and 20 °C.

Table 7.3 System Parameters Used in Model Predictions

System Parameters	Event 5		Event 6	
	MH8	MH7	MH8	MH7
drop height D (m)	3	1.4	3	1.4
weir depth H (m)	0.24	0.24	0.23	0.23
wastewater flowrate Q (m ³ /hr)	720	720	684	684
weir width W (m)	0.9	0.9	0.84	0.84
q (m ³ /m hr)	800	800	814	814
tailwater depth T (m)	0.24	0.24	0.23	0.23
wastewater temp (°C)	15.20	15.20	15.20	15.20

Based on the operating conditions listed in Table 7.3 appropriate values of a,b,c and d were used in the calculation of r_O by implementation of Equations 4 and 5. Calculated individual and total r_O values used in calculating r_{VOC} are presented in Table 7.4.

Table 7.4 Individual and Total r_O Values Used in Model Predictions

	Event 5		Event 6	
	r_O (20 °C)	r_O (15 °C)	r_O (20 °C)	r_O (15 °C)
MH8	2.47	2.29	2.45	2.27
MH7	1.70	1.63	1.70	1.63
Total	4.20	3.73	4.17	3.70

Predicted compound stripping efficiencies for Event 5 and 6 (using Equations 13 and 15) were then estimated by use of r_O (total) values in Table 7.4 and compound specific ϕ_M values obtained from equation 10. When possible, H_C values were obtained from Ashworth *et al.* (1988). Estimation of H_C values for compounds not included in Ashworth

et al. were obtained by vapor pressure and water solubility data. Vapor pressures were obtained from Perry (1984), while solubility estimates were determined using an estimation technique based on chemical structure described in Lyman *et al.* (1982).

A comparison of measured and predicted stripping efficiencies for Event 5 and 6 is presented in Table 7.5. During Event 5, the model underpredicted liquid stripping efficiencies for all three compounds for both temperatures. Measured/predicted stripping ratios at 15 °C ranged from 1.2 to 1.9 and averaged 1.5 while at 20 °C measured/predicted stripping ratio ranged from 1.0 to 1.5 and averaged 1.2. One possible explanation for these differences is the manner in which the measured percent stripped values were obtained. It has already been stated that these values were initially calculated in order to get an idea of the approximate magnitude of stripping across drop structures. It is conceivable that part or all of the differences between the measured and predicted values could be attributed to errors associated with the estimation of these values discussed earlier. It is also possible that the wastewater temperature was higher than 20 °C. If this were the case then the model would have predicted higher stripping efficiencies thus attaining better agreement with measured values. For example if the wastewater temperature was 25 °C then the measured/predicted ratios for the three compounds would range between 0.9 and 1.3, averaging 1.1. The predicted values were also based on assumptions regarding H, T and W. There is the possibility that these assumptions would impact model results. A preliminary evaluation of the sensitivity of the model to changes in these parameters was performed. For this comparison it was assumed that predicted values of H, T and W were off by $\pm 20\%$. Total r_{20} values calculated using these new values were within $\pm 18\%$ of the original values indicating a limited degree of sensitivity to these parameter values.

Clearly, it is imperative that future liquid stripping events include both a measurement of wastewater temperature and system operating parameters such as tailwater depth to improve

confidence in the model predictions and, during periods of constant wastewater flow, an improved method of obtaining TWACs for use in the determination of measured stripping efficiency values. For periods in which constant wastewater is not present it would be necessary to base stripping efficiencies on average mass flow rates.

Measured stripping values for six of the twelve compounds obtained during Event 6 fell within the stripping efficiency ranges predicted using the 15 and 20 °C temperature range. For three of the six compounds that did not fit the predicted range of stripping values the difference may be attributable to the value of H_C used during model prediction. For cumene, 1,3-diethylbenzene, and 1,4-diethylbenzene the value of H_C used during stripping predictions was estimated using vapour pressure and solubility data. Measured/predicted stripping efficiency ratios at 15 °C ranged from 0.5 to 1.8 and averaged 1.1. Similarly for 20 °C, the range was 0.5 to 1.5 and averaged 0.9.

In addition to the potential problems associated with the estimation of H_C , other sources of error were expected to be present during Event 6 similar to those described earlier for Event 5.

Table 7.5 Comparison of Predicted and Measured Percent Stripped Results

Event	Compound	Composite Wastewater concentration (µg/L)				
		MH9 ave	MH6 ave	Meas. %	Pred. %	Pred. %
				Stripped	Stripped	Stripped
					(15 °C)	(20 °C)
5	Ethylbenzene	1600	980	39	27	33
	m,p-Xylenes	7900	5200	34	28	33
	o-Xylene	3500	2000	43	23	28
6	Toluene	1700	1200	29	27	32
	Tetrachloroethene	26	16	38	38	44
	Ethylbenzene	85	58	32	26	33
	m,p-Xylenes	420	280	33	28	33
	o-Xylene	370	220	41	23	28
	Cumene	75	49	35	36	40
	Propylbenzene	390	240	38	33	38
	3,4 Ethyltoluene	2300	1500	35	33	38
	2 Ethyltoluene	650	420	35	32	37
	1,3,5 Trimethylbenz	860	530	38	27	32
	1,3 Diethylbenzene	41	33	20	39	44
	1,4 Diethylbenzene	70	52	26	39	44

Combining both events the average measured/predicted ratio for 15 °C and 20 °C was 1.2 and 1.0, respectively. Overall the model performed well at predicting the percent liquid stripped. However, the ability of the model to predict differences in stripping efficiency due to compound differences was not established. Lack of verification for this potential of the model may be attributed to the limited number of data available for comparison. Also,

due to the similar magnitudes predicted for all compounds during both events and for both temperatures, it is possible that the errors associated with both the measured and predicted values would not allow an accurate comparison at that level. Before this can be demonstrated there needs to be more data compiled and a concerted effort at reducing errors related to both measured and predicted stripping values.

The purpose of this reasearch was to investigate the potential for emissions of VOCs from operating municipal sewers. To facilitate this goal, sewers representing worst case scenarios were selected for monitoring. These sewers received significant industrial discharges of solvent-laden wastewater, were highly ventilated and contained many hydraulic drop structures known to enhance gas-liquid mass transfer.

The emission rate estimates presented in this thesis are not intended to represent potential emissions from all sewers and should not be used as a means for extrapolating emissions from entire sewer networks. While the emission rate estimates are not intended to represent definitive values, it is believed that they are useful in evaluating the relative significance of emissions from sewers. Upon completion of emissions monitoring of two sites, the emission rate estimates were compared with previously reported wastewater treatment plant emission rates. It was determined that there was a potential for emissions of VOCs from some sewers to be significant relative to treatment facilities.

In addition, examination of potential locations for localized stripping of VOCs within "worst case" sewers was also preformed. During this phase of the study, stripping efficiencies across two drop structures were compared to stripping efficiencies along a section of reach characterized by uniform flow. While the absolute stripping efficiency values obtained for each location were susceptible to many sources of potential error, the numbers should be useful in comparing the two locations on a relative basis. If this is the case, then it is apparent from this comparison that, for sewers similar to the MCI in physical design, the dominant location for stripping may be hydraulic drop structures.

Finally, based on this finding, a model capable of predicting stripping efficiencies across drop structures was developed. This model was based on previous work describing oxygen mass transfer at drop structures and accounted for differences between specific VOCs and oxygen through the use of an adjustment parameter which accounted for compound specific gas and liquid phase resistance to mass transfer. A comparison between measured and predicted stripping efficiencies revealed that the model was capable of predicting values within a factor of 2 of measured values for all compounds, and on average, was within $\pm 20\%$ of measured stripping efficiencies.

It is important to note that the development of the model relied on an assumption of infinite ventilation of the drop structures. Model predicted stripping values for systems which are not infinitely ventilated are expected to overpredict stripping efficiencies and may therefore result in predicted emission rates much higher than actual values. In order to model these systems it is necessary that additional studies on the natural ventilation of sewers be performed.

As stated earlier there were four specific objectives associated with this research. These were:

- 1) to quantify emissions of VOCs from wastewater collection systems (WCSs),
- 2) to assess the relative importance of WCSs as sources of VOC emissions to the atmosphere,
- 3) to determine WCS "hot spots" where the majority of emissions originate, and
- 4) to develop a steady state model capable of predicting VOC stripping at hydraulic drop structures within sewers.

Fulfillment of these objectives resulted in the following conclusions:

- 1) Emission rates of VOCs from well ventilated sewers receiving significant VOC mass loadings have the potential to rival or exceed emission rates from downstream wastewater treatment facilities.
- 2) Along well ventilated sewers, hydraulic drop structures may greatly enhance liquid-gas mass transfer resulting in significant stripping of VOCs at these locations. A comparison of stripping efficiencies between drop structures and a uniform section of reach along the Massey Creek Interceptor indicated the majority of stripping (greater than 95 % of total stripping measured) occurred across two drop structures.
- 3) Stripping efficiency estimates for VOCs across well ventilated drop structures can be predicted using an empirically derived oxygen deficit ratio adjusted to account for both gas and liquid phase resistance to mass transfer. A comparison between predicted and

measured stripping efficiencies utilizing data collected during two liquid sampling events revealed that, on average, the predicted values were within $\pm 20\%$ of the measured values.

If additional research were to be performed utilizing the experimental methodology described in this thesis, the author would recommend consideration of the following suggestions:

- 1) In order to improve the average emission rate estimates determined using headspace gas samples it would be recommended to use manifold restricted passive filling of stainless steel cannisters. The manifolds could be preset so as to allow filling of the cannisters over a considerable time period (e.g. several hours) to alleviate any potential problems associated with estimating emission rates based on periodic headspace grab sampling.
- 2) As a refinement of the liquid sampling protocol, it is recommended that the possibility of continuous sampling using Tedlar bags be investigated. The use of these bags would overcome the problems of time weight averaging several grab samples. Also, because it is possible to fill the bags with zero headspace, any stripping losses occurring during the filling of the glass vials would be avoided. Before bags can be used, however, it would be necessary to ensure that the sampling lines would not clog with debris as happened several times during sampling events.
- 3) Although there was only limited verification of the model developed to predict VOC stripping efficiencies at hydraulic drop structures, the results were favourable. It is suggested that additional liquid sampling events at the Massey Creek Interceptor be performed to further evaluate the model. Also, it is recommended that the addition of a variety of VOCs, covering a wide range of H_C values, to be continually injected upstream of the three large drop structures located at manholes 10, 8 and 7, be investigated. Because

of the presence of "in house" VOCs it would be necessary to use "labelled" compounds. One advantage afforded by the use of "labelled" compounds is that of experimental control. Potential problems associated with time weight averaging of "in house" compound concentrations would be avoided by the injection of VOCs at a constant rate and a predetermined concentration. Use of "labelled" compounds would also allow for sampling of wastewater at the influent of the receiving wastewater treatment facility in order to obtain an estimate of the total fraction lost during transit.

4) Several additional improvements to the experimental procedure designed for model verification are also suggested. These include wastewater temperature measurement and tailwater depth measurement. Also it would be beneficial to obtain wastewater dissolved oxygen measurements at various locations to determine the validity of the use of the equation set forth by Nakasone to predict r_0 .

5) Finally if additional work were to be carried out in an attempt to expand or supplement the information presented in this thesis, the author would suggest examination of the forces involved in natural ventilation of sewers. The high ventilation rates measured at the MCI and the degree of headspace saturation study performed indicated that the MCI could be assumed to be infinitely ventilated. This assumption greatly simplified the development of the stripping efficiency model. Had the sewer not been infinitely ventilated, accumulation in the headspace could occur, thus reducing liquid to gas mass transfer, and subsequently reducing both emissions from the sewer and stripping efficiencies at drop structures. It is recommended that work be done studying sewer ventilation rates in order to ascertain the dominant factors involved in generating natural ventilation. Future work should include the measurement of ventilation rates using SF₆, wastewater flowrates, and barometric and temperature gradients along operating sewers with various numbers and types of gas exchange openings. The development of an algorithm capable of predicting sewer specific

ventilation rate based on measurable parameters such as wastewater flowrate or area of openings for gas exchange could then be incorporated into the stripping efficiency model developed in this thesis to model systems that are not infinitely ventilated.

11. REFERENCES

Apted, R.W., and P. Novak, "Some Studies of Oxygen Uptake at Weirs," Proceedings of the XV Congress. International Association of Hydraulics Research, Paper B23, 177 (1973).

Ashworth, R.A., G.B. Howe, M.E. Mullins and T.N. Rogers, "Air-Water Partitioning Coefficients of Organics in Dilute Aqueous Solutions," Journal of Hazardous Materials, 18: 25, (1988).

Avery, S.T., and P. Novak, "Oxygen Transfer at Hydraulic Structures," Journal of the Hydraulic Division, ASCE, 104: 1521, (1978).

Barsky, J.B., S.S.Q. Hee, S. Clark and J.H.R. Trapp, "Simultaneous Multi-instrument Monitoring of Vapours in Sewer Headspace by Several Direct Reading Instruments," Environmental Research, 39: 307, (1986).

Bell, J.P., I. Osinga and H.R. Melcer, Investigation of Stripping of Volatile Organic Contaminants in Municipal Wastewater Treatment Systems: Phase 1, Report to the Ontario Ministry of the Environment, (1988).

Blackburn, J.W., "Prediction of Organic Chemical Fates in Biological Wastewater Treatment Processes," Environmental Progress, 6 (4): 217, (1987).

Chang, D.P.Y., Schroeder, E.D., and R.L. Corsi, Emissions of Volatile and Potentially Toxic Organic Compounds from Sewage Treatment Plants and Collection Systems, A5-127-32, California Air Resources Board, Sacramento, California, (1987).

Corsi, R.L., and T.R. Card, "Estimation of Air Toxics Emissions Using the Baste Model," Environmental Progress, 10 (4): 290, (1991).

Corsi, R.L., D.P.Y. Chang and E.D. Schroeder, "Assessment of the Effect of Ventilation Rates on VOC Emissions from Sewers," Proceedings of the 82nd Annual Meeting of the Air and Waste Management Association, Anaheim, California, (1989), paper 89-10.5.

Corsi, R.L., J. Shepherd, J. Kemp, C. Quigley, P. Martos, and H.R. Melcer, "VOC Emissions from Small Sewer Drop Structures," in Proceedings of the 86th Annual Meeting of the Air and Waste Management Association, Denver, Colorado (1993).

Corsi, R.L. and A. Whitmore, "Municipal and Industrial Wastewater Collection Systems as Sources of VOC Emissions," Proceedings of the 9th World Clean Air Congress, Montreal, Quebec, (1992), paper IU-15.02.

Dobbins, W.E., "Mechanism of Gas Absorption by Turbulent Liquids", in Advances in Water Pollution Research, Vol. 2, W.W. Eckenfelder ed., Pergamon Press Ltd., New York, pp 61-96, 1962.

Dunovant, V.S., C.S. Clark, S.S.Q. Hee, V.S. Hertzberg and J.H.R. Trapp, "Volatile Organics in the Wastewater and Airspaces of Three Wastewater Treatment Plants," Journal of the Water Pollution Control Federation, **58**: 886, (1986).

Govind, R., L. Lei and R. Dobbs, "Integrated Model for Predicting the Fate of Organics in Wastewater Treatment Plants," Environmental Progress, **10** (1): 13, (1991).

Huang, J.Y.C., G.E. Wilson and T.W. Schroepfer, "Evaluation of Activated Carbon Adsorption for Sewer Odor Control," Journal of the Water Pollution Control Federation, **51** (5): 1054, (1979).

Hsieh, C.C., R.W. Babcock, and M.K. Stenstrom, "Estimating Semi-volatile Organic Compound Emission Rates and Oxygen Transfer Coefficients in Diffused aeration," presented at the 65th Annual Conference of the Water Environment Federation, New Orleans, Louisiana, (1992).

Lyman, J.L., W.F. Reehl, and D.H.R. Rosenblatt, Handbook of Chemical Property Estimation Methods, American Chemical Society, Washington, D.C., (1982)

MacKay, D., W.Y. Shiu and K.C. Ma, Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Volume 1: Monoaromatic Hydrocarbons, Chlorobenzenes and PCB's, Lewis Publishers Inc., Chelsea, Michigan, 1992.

McLachlin, M., D. Mackay and P.H.R. Jones, "A Conceptual Model of Organic Chemical Volatilization at Waterfalls," Environmental Science and Technology, **24**: 252, (1990).

Mihelcic, J.R., C.R. Baillod, J.C. Crittenden and T.N. Rogers. "Estimation of VOC Emissions from Wastewater Facilities by Volatilization and Stripping," Journal of the Air and Waste Management Association, **43**: 97, (1993).

Nakasone, H.R., "Study of Aeration at Weirs and Cascades," Journal of Environmental Engineering, ASCE, **113** (1): 64, (1986).

Namkung, E. and B.E. Rittman, "Estimating Volatile Organic Compound Emissions from Publically Owned Treatment Works," Journal of the Water Pollution Control Federation, **59** (7): 670, (1987).

Perry, R.H.R., and D. Green, eds., Perry's Chemical Engineers Handbook, 6th Ed., McGraw-Hill Inc. New York, (1984).

Pescod, M.B., and A.C. Price, "Fundamentals of Sewer Ventilation as Applied to the Tyneside Sewerage Scheme," Water Pollution Control, **90** (1): 385, (1981).

Pescod, M.B., and A.C. Price, "Major Factors in Sewer Ventilation," Journal of the Water Pollution Control Federation, **54**, 385, (1982).

Pincince, A..B., "Transfer of Oxygen and Emissions of Volatile Organic Compounds at Clarifier Weirs," Research Journal of the Water Pollution Control Federation, **63** (2): 114, (1991).

Reid, J.M. and M. McEvoy, "Monitoring Sewer Atmospheres for Organic Vapours", Journal of the Inst. of Water & Env. Mgmt., **1** (2): 161, (1987).

Thistlewayte, D.K.B. (Ed.), The Control of Sulphides in Sewerage Systems, Ann Arbor Science Publishers, Ann Arbor, (1972).

APPENDIX A: FLOWRATE MEASUREMENT VERIFICATION

The HWA method of flowrate measurement was compared to both a timed volume displacement technique and a concentration dilution technique. These two techniques are briefly described below.

Timed volume displacement method. The flowrate is measured by determining the time required to fill a bag of known volume. To use this method the volume of the bag to be used had to be first determined. This was done by filling the bag with a calibrated air pump and noting the time required to fill the bag.

Concentration dilution method. This was performed by injecting a known concentration of carbon monoxide at a known flowrate into the barrel through a tube inserted through one of the 1" diameter holes. At another hole the concentration of the carbon monoxide exiting the barrel was measured using a portable carbon monoxide detector. The air flowrate was then calculated by performing a mass balance on the carbon monoxide (assuming no losses). Flowrate measurements obtained using carbon monoxide were performed with the entire apparatus placed inside an operating fume hood. This was done to ensure minimal exposure to carbon monoxide.

To compare the different flowrate measurement methods a large plastic drum (approximately 45 US gal. in size) was used. The plastic drum was modified to allow air movement through the drum by drilling 14 1" diameter circular holes around the periphery of the top. A blower was attached to one of the threaded portholes located on the bottom. Different flowrates were then achieved by sealing varying numbers of the 1" holes with duct tape. Three different flowrates were measured. In part 1 two holes were left uncovered. In parts 2 and 3, four and six holes were left uncovered, respectively.

RESULTS:

Bag volume determination:

Flowrate used was 5 L/min

Time to fill bag:

Trial 1: 6.5 min.

Trial 2: 6.75 min.

Ave time: 6.6 min.

Volume of bag = 5 L/min * 6.6 min = 33 L.

Part 1: 2 holes left uncovered.

Timed volume displacement results:

Bag filled from hole #12.

Trial 1: 12.3 sec

Trial 2: 12.9 sec

Trial 3: 12.6 sec

Ave. time: 12.6 sec

Flowrate from hole #12 = 33 L/12.6 sec = 2.62 L/sec.

HWA flowrate measurement results:

HWA measurements from hole #12

Ave. vel. = 5.5 m/s

Area = 0.00051 m²

Flowrate from hole #12 = 5.5 m/s * 0.00051 m² = 2.81 L/s.

Part 2: 4 holes left uncovered.

Timed volume displacement results:

Bag filled from hole #12.

Trial 1: 16.3 sec

Trial 2: 15.3 sec

Trial 3: 16.2 sec

Trial 4: 15.5 sec

Ave. time: 15.8 sec

Flowrate from hole #12 = $33 \text{ L} / 15.8 \text{ sec} = 2.09 \text{ L/sec}$.

HWA flowrate measurement results:

HWA measurements from hole #12

Ave. vel. = 3.9 m/s

Area = 0.00051 m^2

Flowrate from hole #12 = $3.9 \text{ m/s} * 0.00051 \text{ m}^2 = 1.99 \text{ L/s}$.

Part 3: 6 holes left uncovered.

Timed volume displacement results:

Bag filled from hole #12.

Trial 1: 21.8 sec

Trial 2: 21.3 sec

Trial 3: 20.0 sec

Trial 4: 22.6 sec

Ave. time: 21.4 sec

Flowrate from hole #12 = $33 \text{ L} / 21.4 \text{ sec} = 1.54 \text{ L/sec}$.

HWA flowrate measurement results:

HWA measurements from hole #12

Ave. vel. = 3.1 m/s

Area = 0.00051 m^2

Flowrate from hole #12 = $3.1 \text{ m/s} * 0.00051 \text{ m}^2 = 1.58 \text{ L/s}$.

Concentration dilution method results:

Injected 99.5% pure CO (995000ppm) at 32.8 mL/min.

CO exit concentration measured at hole #12 = 63 ppm

Mass CO in = Mass CO out

$950000 \text{ ppm} * 32.8 \text{ mL/min} = 63 \text{ ppm} * Q \text{ total out}$

$Q \text{ total out} = (995000 \text{ ppm} * 32.8 \text{ mL/min}) / 63 \text{ ppm}$

$Q \text{ total out} = 8.63 \text{ L/sec}$

Flowrate from hole #12 = $8.63 \text{ L/sec} / 6 = 1.44 \text{ L/sec}$

Summary of results:

Part:	Timed volume displacement	Hole #12 Flowrate (L/sec)	
		HWA method	Conc. dilution
1	2.6	2.8	
2	2.1	2.0	
3	1.5	1.6	1.4

The consistently similar results for the HWA and timed volume displacement technique during Part 1, 2 and 3 and the similar results for all three measurement techniques in Part 3 indicate that use of the HWA measurement is valid.

***APPENDIX B: MASSEY CREEK INTERCEPTOR
EMISSIONS MONITORING DATA***

Table B.1. MCI Events 1 - 4: Ventilation Data.

Event 1					
Time	MH 7	MH 6	Ventilation (m ³ /s)		Total
9:00	0.09	0.11	MH 5	MH 3	0.41
11:00	0.11	0.14	0.10	0.12	0.51
13:00	0.12	0.17	0.14	0.08	0.51
15:00	0.08	0.12	0.09	0.08	0.37
16:00	0.08	0.11	0.09	0.11	0.39
Event 2					
Time	MH 7	MH 6	Ventilation (m ³ /s)		Total
8:00	0.09	0.10	MH 5	MH 3	0.37
9:15	0.10	0.07	0.08	0.10	0.37
10:30	0.11	0.13	0.11	0.10	0.45
11:45	0.13	0.17	0.16	0.17	0.63
13:30	0.17	0.16	0.16	0.16	0.65
14:15	0.12	0.15	0.16	0.11	0.54
15:30	0.10	0.16	0.16	0.12	0.54
Event 3					
Time	MH 7	MH 6	Ventilation (m ³ /s)		Total
9:00	0.09	0.09	MH 5	MH 3	0.36
13:00	0.12	0.11	0.11	0.07	0.43
16:00	0.09	0.11	0.12	0.08	0.43
			0.10	0.07	0.37
Event 4					
Time	MH 7	MH 6	Ventilation (m ³ /s)		Total
6:00			MH 5	MH 3	
8:00				0.06	
9:00	0.11	0.09	0.14	0.11	0.45
10:00	0.10	0.14	0.12	0.13	0.49
11:00	0.16	0.19	0.11	0.15	0.61
12:00	0.14	0.13	0.17	0.16	0.60
13:00	0.13	0.10	0.15	0.15	0.53
14:00	0.07	0.15	0.16	0.14	0.52
15:00	0.11	0.13	0.12	0.13	0.49
16:00	0.11	0.14	0.15	0.15	0.55
17:00				0.13	
18:00				0.13	
19:00				0.11	
20:00				0.10	
22:00				0.11	
24:00				0.10	
2:00				0.06	
4:00				0.05	
6:00				0.04	

Table B.2. MCI Event 1 Emissions Monitoring Data.

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
Toluene	9:00	7	30	0.09	9.6
		6	42	0.11	16
		5	35	0.10	13
		3	31	0.11	12
	13:00	7	129	0.12	56
		6	53	0.17	21
		5	76	0.14	38
		3	50	0.08	14
	16:00	7	74	0.08	21
		6	123	0.11	49
		5	80	0.09	26
		3	50	0.11	20
Ethylbenzene	9:00	7	5.0	0.09	1.6
		6	7.1	0.11	2.9
		5	5.8	0.10	2.1
		3	5.3	0.11	2.1
	13:00	7	5.9	0.12	2.5
		6	3.0	0.17	1.8
		5	4.1	0.14	2.1
		3	2.7	0.08	0.8
	16:00	7	11	0.08	3.1
		6	14	0.11	5.6
		5	8.9	0.09	2.9
		3	6.9	0.11	2.7
Total Xylenes	9:00	7	1.5	0.09	0.5
		6	2.1	0.11	0.8
		5	1.8	0.10	0.7
		3	1.6	0.11	0.6
	13:00	7	1.7	0.12	0.7
		6	1.2	0.17	0.7
		5	1.3	0.14	0.7
		3	1.1	0.08	0.3
	16:00	7	2.7	0.08	0.8
		6	3.7	0.11	1.5
		5	2.6	0.09	0.8
		3	2.1	0.11	0.8
Tetrachloroethene	9:00	7	0.8	0.09	0.3
		6	1.1	0.11	0.4
		5	0.9	0.10	0.3
		3	0.9	0.11	0.4
	13:00	7	0.9	0.12	0.4
		6	0.6	0.17	0.4
		5	0.7	0.14	0.4
		3	0.7	0.08	0.2
	16:00	7	2.4	0.08	0.7
		6	3.9	0.11	1.6
		5	3.0	0.09	1.0
		3	2.2	0.11	0.9

Table B.3. MCI Event 2: Emissions Monitoring Data.

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
Toluene	8:00	7	6.5	0.09	2.1
		6	5.4	0.10	1.9
		5	3.2	0.08	0.9
		3	3.7	0.10	1.4
	10:30	7	46	0.11	18
		6	71	0.13	33
		5	89	0.11	35
		3	56	0.10	20
	15:30	7	16	0.10	5.9
		6	25	0.16	14
		5	33	0.16	19
		3	46	0.12	20
Ethylbenzene	8:00	7	0.3	0.09	0.1
		6	0.2	0.10	0.1
		5	1.3	0.08	0.4
		3	1.3	0.10	0.5
	10:30	7	6.6	0.11	2.6
		6	9.6	0.13	4.5
		5	9.5	0.11	3.8
		3	6.3	0.10	2.3
	15:30	7	0.9	0.10	0.3
		6	1.5	0.16	0.9
		5	5.4	0.16	3.1
		3	3.4	0.12	1.5
Total Xylenes	8:00	7	4.0	0.09	1.3
		6	2.4	0.10	0.9
		5	8.0	0.08	2.3
		3	10	0.10	3.8
	10:30	7	26	0.11	10
		6	36	0.13	17
		5	51	0.11	13
		3	32	0.10	12
	15:30	7	14	0.10	5.0
		6	17	0.16	10
		5	30	0.16	18
		3	24	0.12	11
Tetrachloroethene	8:00	7	0.2	0.09	0.1
		6	0.2	0.10	0.1
		5	BMDL	0.08	NA
		3	0.1	0.10	0
	10:30	7	0.3	0.11	0.1
		6	0.5	0.13	0.2
		5	0.6	0.11	0.2
		3	0.3	0.10	0.1
	15:30	7	0.8	0.10	0.3
		6	1.8	0.16	1.0
		5	2.2	0.16	1.3
		3	3.2	0.12	1.4

BMDL: Below Method Detection Limit (< 0.1 mg/m³).

NA: Not Applicable.

Table B.4. MCI Event 3: Emissions Monitoring Data.

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
Toluene	9:00	7	BMDL	0.09	NA
		6	BMDL	0.09	NA
		5	BMDL	0.11	NA
		3	BMDL	0.07	NA
	13:00	7	BMDL	0.12	NA
		6	BMDL	0.11	NA
		5	BMDL	0.12	NA
		3	BMDL	0.08	NA
	16:00	7	BMDL	0.09	NA
		6	BMDL	0.11	NA
		5	BMDL	0.10	NA
		3	BMDL	0.07	NA
Ethylbenzene	9:00	7	BMDL	0.09	NA
		6	BMDL	0.09	NA
		5	BMDL	0.11	NA
		3	BMDL	0.07	NA
	13:00	7	BMDL	0.12	NA
		6	BMDL	0.11	NA
		5	BMDL	0.12	NA
		3	BMDL	0.08	NA
	16:00	7	BMDL	0.09	NA
		6	BMDL	0.11	NA
		5	BMDL	0.10	NA
		3	BMDL	0.07	NA
Total Xylenes	9:00	7	BMDL	0.09	NA
		6	BMDL	0.09	NA
		5	BMDL	0.11	NA
		3	BMDL	0.07	NA
	13:00	7	BMDL	0.12	NA
		6	BMDL	0.11	NA
		5	BMDL	0.12	NA
		3	BMDL	0.08	NA
	16:00	7	BMDL	0.09	NA
		6	BMDL	0.11	NA
		5	BMDL	0.10	NA
		3	BMDL	0.07	NA
Tetrachloroethene	9:00	7	0.2	0.09	0.1
		6	BMDL	0.09	NA
		5	BMDL	0.11	NA
		3	0.5	0.07	0.1
	13:00	7	1.0	0.12	0.4
		6	0.7	0.11	0.3
		5	1.0	0.12	0.4
		3	2.9	0.08	0.8
	16:00	7	2.6	0.09	0.8
		6	0.4	0.11	0.2
		5	1.9	0.10	0.7
		3	2.0	0.07	0.5

BMDL: Below Method Detection Limit (< 0.1 mg/m³).

NA: Not Applicable.

Table B.5. MCI Event 4: Emissions Monitoring Data at Manhole 3.

Compound	Time	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
Toluene	6:00	52	0.06	12
	8:00	16	0.11	5.8
	10:00	57	0.13	26
	12:00	170	0.16	100
	14:00	176	0.14	88
	16:00	140	0.15	76
	18:00	152	0.13	70
	20:00	36	0.10	13
	22:00	124	0.11	49
	24:00	44	0.10	16
	2:00	11	0.06	2.3
	4:00	14	0.05	2.4
	6:00	3.6	0.04	0.6
Ethylbenzene	6:00	12	0.06	2.6
	8:00	6.7	0.11	2.5
	10:00	4.7	0.13	2.2
	12:00	9.2	0.16	5.4
	14:00	7.8	0.14	3.9
	16:00	14	0.15	7.9
	18:00	18	0.13	8.3
	20:00	9.4	0.10	3.3
	22:00	22	0.11	8.7
	24:00	5.0	0.10	1.7
	2:00	3.3	0.06	0.7
	4:00	2.5	0.05	0.5
	6:00	1.9	0.04	0.2
Tetrachloroethene	6:00	0.2	0.06	0
	8:00	ND	0.11	NA
	10:00	0.3	0.13	0.1
	12:00	12	0.16	7.3
	14:00	1.1	0.14	0.6
	16:00	1.0	0.15	0.6
	18:00	0.6	0.13	0.2
	20:00	0.6	0.10	0.2
	22:00	0.5	0.11	0.2
	24:00	0.4	0.10	0.1
	2:00	ND	0.06	NA
	4:00	0.1	0.05	0
	6:00	ND	0.04	NA

Table B.5. MCI Event 4: Emissions Monitoring Data at Manhole 3
(cont.).

Compound	Time	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
m,p - Xylenes	6:00	72	0.06	16
	8:00	47	0.11	18
	10:00	39	0.13	18
	12:00	59	0.16	35
	14:00	54	0.14	27
	16:00	122	0.15	66
	18:00	118	0.13	54
	20:00	65	0.10	23
	22:00	138	0.11	54
	24:00	43	0.10	15
	2:00	25	0.06	5.1
	4:00	19	0.05	3.3
	6:00	12	0.04	1.7
o - Xylene	6:00	20	0.06	4.6
	8:00	8.3	0.11	3.2
	10:00	9.9	0.13	4.5
	12:00	10	0.16	5.8
	14:00	12	0.14	6.1
	16:00	31	0.15	17
	18:00	29	0.13	13
	20:00	18	0.10	6.2
	22:00	35	0.11	14
	24:00	9.6	0.10	3.4
	2:00	4.7	0.06	0.9
	4:00	4.4	0.05	0.8
	6:00	2.6	0.04	0.3
Benzene	6:00	ND	0.06	NA
	8:00	ND	0.11	NA
	10:00	6.6	0.13	3.0
	12:00	15	0.16	8.6
	14:00	4.2	0.14	2.2
	16:00	12	0.15	6.3
	18:00	37	0.13	17
	20:00	ND	0.10	NA
	22:00	ND	0.11	NA
	24:00	2.3	0.10	0.8
	2:00	8.2	0.06	1.7
	4:00	15	0.05	2.6
	6:00	4.2	0.04	0.6

Table B.6. MCI Event 4: TNMHC Concentration Data.

Time	Concentration (ppm Toluene equiv.)				Average
	MH 7	MH 6	MH 5	MH 3	
8:00	17	18	18	17	18
9:00	83	95	93	90	90
10:00	41	42	43	45	43
11:00	29	29	27	26	28
12:00	54	47	54	59	54
13:00	99	85	97	87	92
14:00	70	98	90	87	86
15:00	109	95	89	89	96
16:00	62	56	55	60	58

Table B.7. MCI Event 4: TNMHC Emissions Data at Manhole 3

Time	Conc. ¹ (ppm)	Conc. ² (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
6:00	32	122	0.06	26
8:00	17	65	0.11	26
10:00	45	172	0.13	80
12:00	59	226	0.16	130
14:00	87	333	0.14	168
16:00	60	230	0.15	124
18:00	89	341	0.13	160
20:00	36	138	0.10	50
22:00	75	287	0.11	114
24:00	28	107	0.10	38
2:00	11	42	0.06	9.0
4:00	6	23	0.05	4.1
6:00	6	23	0.04	3.3

1. Concentration expressed in toluene equivalents.
2. Concentration conversion performed assuming 20 °C.

APPENDIX C: HIGH PARK EMISSIONS MONITORING DATA

Table C.1. HP Event 1: Emissions Monitoring Data.

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
Toluene	8:00	1	8.4	0.05	1.6
		2	ND	0.05	NA
		3	9.6	0.04	1.4
	9:30	1	24	0.07	5.8
		2	3.2	0.08	0.9
		3	1.0	0.05	0.2
	11:00	1	1.2	0.06	0.3
		2	ND	0.09	NA
		3	ND	0.10	NA
	12:30	1	7.8	0.09	2.6
		2	12	0.07	3.2
		3	11	0.09	3.4
	14:00	1	ND	0.08	NA
		2	2.7	0.09	0.8
		3	6.0	0.05	1.0
	15:30	1	0.9	0.11	0.4
		2	3.6	0.10	1.4
		3	2.1	0.09	0.7
Ethylbenzene	8:00	1	2.2	0.05	0.4
		2	ND	0.05	NA
		3	2.3	0.04	0.3
	9:30	1	12	0.07	2.7
		2	ND	0.08	NA
		3	ND	0.05	NA
	11:00	1	0.3	0.06	NA
		2	ND	0.09	NA
		3	ND	0.10	NA
	12:30	1	ND	0.09	NA
		2	ND	0.07	NA
		3	0.4	0.09	0.1
	14:00	1	ND	0.08	NA
		2	ND	0.09	NA
		3	0.8	0.05	0.1
	15:30	1	ND	0.11	NA
		2	ND	0.10	NA
		3	ND	0.09	NA
m,p - Xylenes	8:00	1	13	0.05	2.5
		2	0.2	0.05	0
		3	14	0.04	2.1
	9:30	1	41	0.07	9.7
		2	0.9	0.08	0.3
		3	0.1	0.05	0
	11:00	1	4.3	0.06	0.9
		2	0.2	0.09	0
		3	ND	0.10	NA
	12:30	1	3.7	0.09	1.3
		2	5.3	0.07	1.4
		3	5.6	0.09	1.8
	14:00	1	0.9	0.08	0.3
		2	0.7	0.09	0.2
		3	7.8	0.05	1.3
	15:30	1	0.4	0.11	0.2
		2	2.0	0.10	0.7
		3	2.7	0.09	0.9

Table C.1. HP Event 1: Emissions Monitoring Data (cont.).

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
o - Xylene	8:00	1	6.7	0.05	1.3
		2	ND	0.05	NA
		3	6.9	0.04	1.0
	9:30	1	22	0.07	5.1
		2	0.2	0.08	0
		3	ND	0.05	NA
	11:00	1	1.6	0.06	0.4
		2	ND	0.09	NA
		3	ND	0.10	NA
	12:30	1	4.0	0.09	1.4
		2	5.7	0.07	1.5
		3	5.3	0.09	1.7
	14:00	1	1.4	0.08	0.4
		2	0.4	0.09	0.1
		3	13	0.05	2.2
	15:30	1	0.3	0.11	0.1
		2	2.8	0.10	1.0
		3	3.8	0.09	1.3
EMB ¹	8:00	1	21	0.05	3.9
		2	ND	0.05	NA
		3	20	0.04	2.9
	9:30	1	56	0.07	14
		2	1.2	0.08	0.4
		3	ND	0.05	NA
	11:00	1	5.0	0.06	1.1
		2	0.1	0.09	0
		3	ND	0.10	NA
	12:30	1	49	0.09	16
		2	61	0.07	16
		3	53	0.09	17
	14:00	1	7.0	0.08	2.1
		2	10	0.09	3.1
		3	54	0.05	8.8
	15:30	1	2.9	0.11	1.1
		2	15	0.10	5.5
		3	18	0.09	6.1
Trimethylbenzene	8:00	1	4.2	0.05	0.8
		2	ND	0.05	NA
		3	4.5	0.04	0.6
	9:30	1	15	0.07	3.5
		2	ND	0.08	NA
		3	ND	0.05	NA
	11:00	1	0.5	0.06	0
		2	ND	0.09	NA
		3	ND	0.10	NA
	12:30	1	14	0.09	4.7
		2	16	0.07	2.1
		3	13	0.09	4.3
	14:00	1	1.2	0.08	0.3
		2	1.1	0.09	0.3
		3	14	0.05	2.3
	15:30	1	0.2	0.11	0
		2	2.4	0.10	0.9
		3	3.7	0.09	1.3

1. EMB - Ethylmethylbenzene

Table C.2 HP Event 2: Emissions Monitoring Data.

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
Toluene	8:00	1	1.0	0.09	0.3
		2	0.7	0.10	0.3
		3	0.2	0.06	0
	9:30	1	0.4	0.10	0.1
		2	0.3	0.10	0.1
		3	ND	0.09	NA
	11:00	1	0.4	0.12	0.2
		2	0.2	0.15	0.1
		3	0.1	0.10	0
	12:30	1	0.2	0.12	0.1
		2	ND	0.15	NA
		3	ND	0.11	NA
	14:00	1	1.0	0.07	0.2
		2	ND	0.05	NA
		3	0.1	0.08	0
	15:30	1	1.1	0.14	0.5
		2	0.7	0.13	0.3
		3	ND	0.13	NA
m,p - Xylene	8:00	1	0.3	0.09	0.1
		2	0.2	0.10	0.1
		3	0.1	0.06	0
	9:30	1	0.2	0.10	0.1
		2	0.1	0.10	0
		3	ND	0.09	NA
	11:00	1	0.4	0.12	0.2
		2	0.2	0.15	0.1
		3	0.1	0.10	0
	12:30	1	0.1	0.12	0
		2	ND	0.15	NA
		3	ND	0.11	NA
	14:00	1	0.3	0.07	0.1
		2	ND	0.05	NA
		3	ND	0.08	NA
	15:30	1	0.4	0.14	0.2
		2	0.2	0.13	0.1
		3	ND	0.13	NA
o - Xylene	8:00	1	0.1	0.09	0
		2	0.1	0.10	0
		3	ND	0.06	NA
	9:30	1	0.1	0.10	0
		2	0.1	0.10	0
		3	ND	0.09	NA
	11:00	1	0.2	0.12	0.1
		2	0.1	0.15	0
		3	0.1	0.10	0
	12:30	1	ND	0.12	NA
		2	ND	0.15	NA
		3	ND	0.11	NA
	14:00	1	0.2	0.07	0
		2	ND	0.05	NA
		3	ND	0.08	NA
	15:30	1	0.2	0.14	0.1
		2	0.1	0.13	0
		3	ND	0.13	NA

Table C.2 HP Event 2: Emissions Monitoring Data (cont.).

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
Trichloroethene	8:00	1	0.9	0.09	0.3
		2	0.5	0.10	0.2
		3	0.3	0.06	0.1
	9:30	1	0.5	0.10	0.2
		2	0.4	0.10	0.1
		3	0.2	0.09	0.1
	11:00	1	0.5	0.12	0.2
		2	0.5	0.15	0.3
		3	0.5	0.10	0.2
	12:30	1	0.5	0.12	0.2
		2	ND	0.15	NA
		3	ND	0.11	NA
	14:00	1	0.7	0.07	0.2
		2	ND	0.05	NA
		3	0.2	0.08	0
	15:30	1	0.6	0.14	0.3
		2	0.6	0.13	0.3
		3	0.1	0.13	0.1
Tetrachloroethene	8:00	1	0.4	0.09	0.1
		2	0.5	0.10	0.2
		3	0.2	0.06	0
	9:30	1	0.5	0.10	0.2
		2	0.3	0.10	0.1
		3	0.2	0.09	0
	11:00	1	0.4	0.12	0.2
		2	0.4	0.15	0.2
		3	0.3	0.10	0.1
	12:30	1	0.4	0.12	0.2
		2	ND	0.15	NA
		3	ND	0.11	NA
	14:00	1	0.3	0.07	0.1
		2	ND	0.05	NA
		3	ND	0.08	NA
	15:30	1	0.3	0.14	0.1
		2	0.3	0.13	0.1
		3	0.1	0.13	0
EMB ¹	8:00	1	0.2	0.09	0.1
		2	0.1	0.10	0
		3	0.1	0.06	0
	9:30	1	0.1	0.10	0
		2	0.2	0.10	0.1
		3	ND	0.09	NA
	11:00	1	0.3	0.12	0.1
		2	0.1	0.15	0.1
		3	0.1	0.10	0
	12:30	1	0.1	0.12	0
		2	ND	0.15	NA
		3	ND	0.11	NA
	14:00	1	0.2	0.07	0
		2	ND	0.05	NA
		3	ND	0.08	NA
	15:30	1	0.2	0.14	0.1
		2	0.2	0.13	0.1
		3	ND	0.13	NA

1. EMB - ethylmethylbenzene

Table C.3 HP Event 3: Emissions Monitoring Data.

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
Toluene	8:00	1	ND	0.07	NA
		2	ND	0.07	NA
		3	ND	0.07	NA
	9:30	1	ND	0.09	NA
		2	ND	0.08	NA
		3	ND	0.05	NA
		4	ND	0.04	NA
		5	ND	0.14	NA
	11:00	1	25	0.02	1.5
		2	6.6	0.07	1.7
		3	ND	0.07	NA
	12:30	1	5.8	0.11	2.4
		2	ND	0.10	NA
		3	ND	0.11	NA
		4	8.6	0.03	0.8
		5	10	0.13	4.7
	14:00	1	2.6	0.05	0.5
		2	ND	0.06	NA
		3	ND	0.05	NA
		4	1.6	0.03	0.2
		5	2.3	0.12	1.0
	15:30	1	7.6	0.06	1.5
		2	7.9	0.04	1.1
		3	19	0.06	4.5
Ethylbenzene	8:00	1	ND	0.07	NA
		2	ND	0.07	NA
		3	ND	0.07	NA
	9:30	1	ND	0.09	NA
		2	ND	0.08	NA
		3	ND	0.05	NA
		4	ND	0.04	NA
		5	ND	0.14	NA
	11:00	1	1.5	0.02	0.1
		2	0.1	0.07	0
		3	ND	0.07	NA
	12:30	1	0.5	0.11	0.2
		2	ND	0.10	NA
		3	ND	0.11	NA
		4	1.0	0.03	0.1
		5	1.0	0.13	0.5
	14:00	1	0.2	0.05	0
		2	ND	0.06	NA
		3	ND	0.05	NA
		4	0.1	0.03	0
		5	0.1	0.12	0
	15:30	1	1.0	0.06	0.2
		2	0.7	0.04	0.1
		3	3.2	0.06	0.7

Table C.3 HP Event 3: Emissions Monitoring Data (cont.).

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
m,p - Xylenes	8:00	1	0.3	0.07	0.1
		2	ND	0.07	NA
		3	0.2	0.07	0
	9:30	1	0.4	0.09	0.1
		2	0.2	0.08	0
		3	0.4	0.05	0.1
		4	ND	0.04	NA
		5	ND	0.14	NA
	11:00	1	6.9	0.02	0.4
		2	1.7	0.07	0.4
		3	0.1	0.07	0
	12:30	1	3.0	0.11	1.3
		2	ND	0.10	NA
		3	ND	0.11	NA
		4	5.3	0.03	0.5
		5	5.2	0.13	2.4
	14:00	1	2.5	0.05	0.5
		2	0.3	0.06	0.1
		3	ND	0.05	NA
		4	2.0	0.03	0.2
		5	2.0	0.12	0.9
	15:30	1	5.5	0.06	1.1
		2	5.7	0.04	0.8
		3	14	0.06	3.3
o - Xylene	8:00	1	ND	0.07	NA
		2	ND	0.07	NA
		3	ND	0.07	NA
	9:30	1	ND	0.09	NA
		2	ND	0.08	NA
		3	ND	0.05	NA
		4	ND	0.04	NA
		5	ND	0.14	NA
	11:00	1	4.5	0.02	0.3
		2	0.9	0.07	0.2
		3	ND	0.07	NA
	12:30	1	7.0	0.11	2.9
		2	ND	0.10	NA
		3	ND	0.11	NA
		4	23	0.03	2.2
		5	23	0.13	10
	14:00	1	11	0.05	2.1
		2	1.3	0.06	0.3
		3	1.0	0.05	0.2
		4	7.7	0.03	0.8
		5	8.3	0.12	3.7
	15:30	1	6.5	0.06	1.3
		2	3.4	0.04	0.4
		3	9.7	0.06	2.2

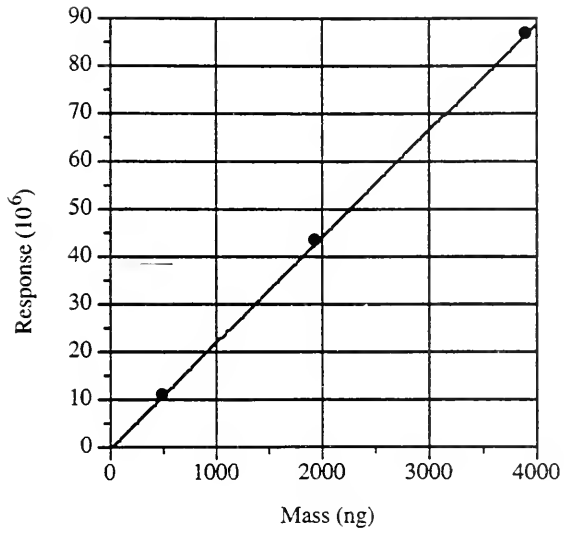
Table C.3 HP Event 3: Emissions Monitoring Data (cont.).

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
EMB ¹	8:00	1	0.1	0.07	0
		2	ND	0.07	NA
		3	ND	0.07	NA
	9:30	1	0.4	0.09	0.1
		2	ND	0.08	NA
		3	0.2	0.05	0
		4	ND	0.04	NA
		5	ND	0.14	NA
	11:00	1	12	0.02	0.7
		2	3.4	0.07	0.9
		3	0.1	0.07	0
	12:30	1	13	0.11	5.1
		2	ND	0.10	NA
		3	ND	0.11	NA
		4	22	0.03	2.2
		5	19	0.13	8.8
	14:00	1	22	0.05	4.2
		2	4.8	0.06	1.1
		3	11	0.05	1.8
		4	19	0.03	1.9
		5	21	0.12	9.2
	15:30	1	19	0.06	3.8
		2	15	0.04	1.9
		3	21	0.06	4.8
Trimethyl benzene	8:00	1	ND	0.07	NA
		2	ND	0.07	NA
		3	ND	0.07	NA
	9:30	1	ND	0.09	NA
		2	ND	0.08	NA
		3	ND	0.05	NA
		4	ND	0.04	NA
		5	ND	0.14	NA
	11:00	1	6.4	0.02	0.4
		2	1.5	0.07	0.4
		3	ND	0.07	NA
	12:30	1	6.8	0.11	2.7
		2	ND	0.10	NA
		3	ND	0.11	NA
		4	16	0.03	1.5
		5	12	0.13	5.5
	14:00	1	13	0.05	2.4
		2	3.2	0.06	0.7
		3	5.1	0.05	0.8
		4	11	0.03	1.1
		5	12	0.12	5.1
	15:30	1	10	0.06	2.1
		2	6.8	0.04	0.9
		3	9.2	0.06	2.2

1. EMB - Ethylmethylbenzene

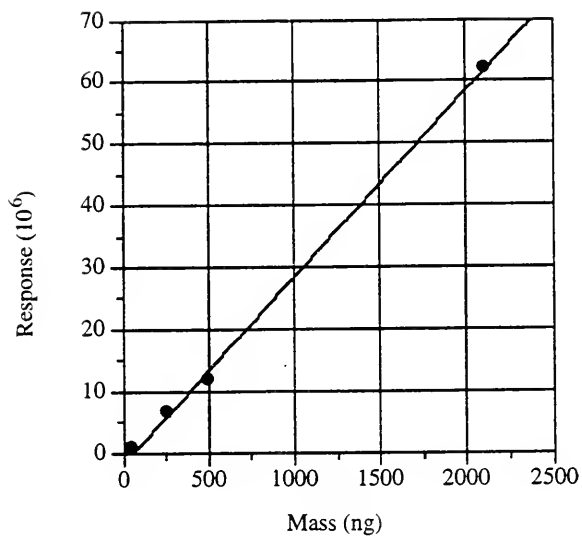
APPENDIX D: EMISSIONS MONITORING CALIBRATION CURVES

Massey Creek Event 1
Toluene Standard Curve



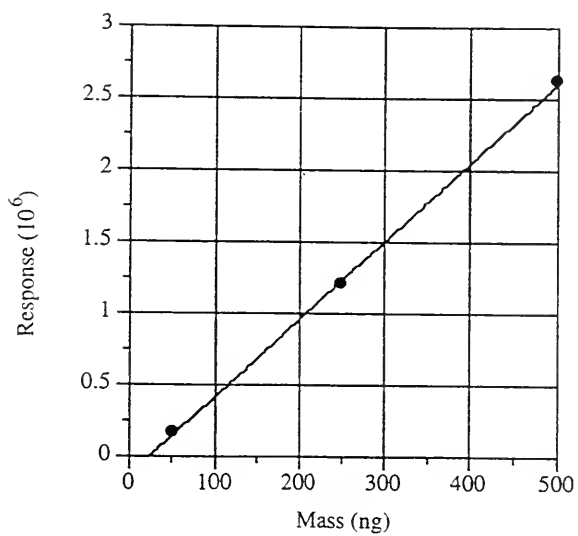
$$R^2 = 0.999$$

Massey Creek Event 1
Ethylbenzene Standard Curve



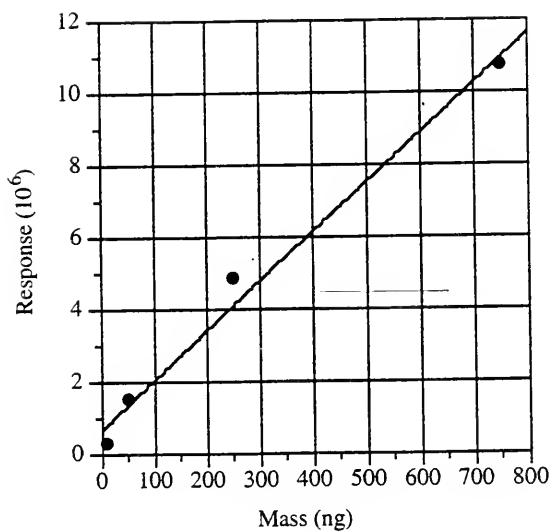
$$R^2 = 0.999$$

Massey Creek Event 1
Tetrachlororethene Standard Curve



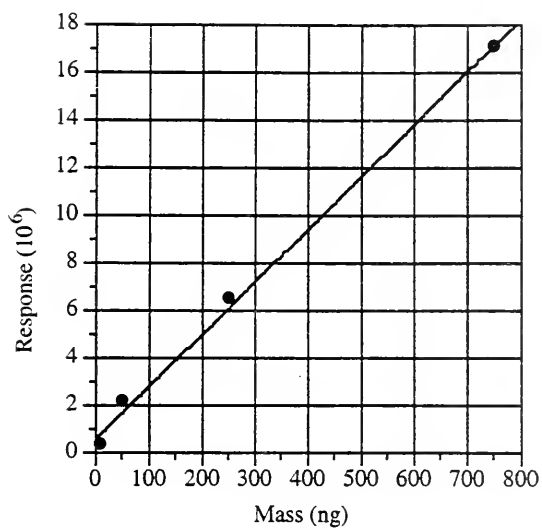
$$R^2 = 0.999$$

Massey Creek Event 2
Toluene Standard Curve



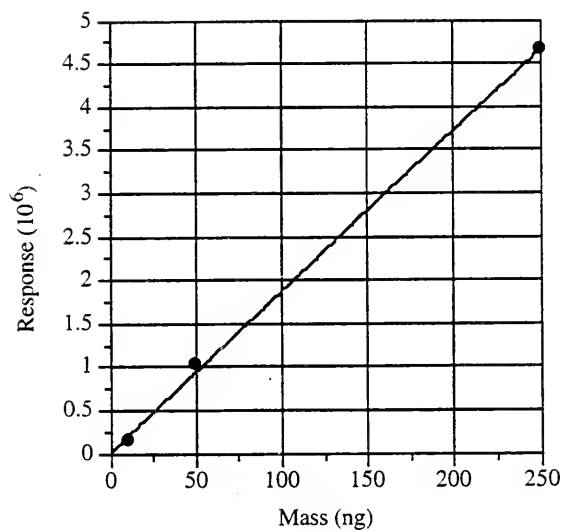
$$R^2 = 0.994$$

Massey Creek Event 2
Ethylbenzene Standard Curve



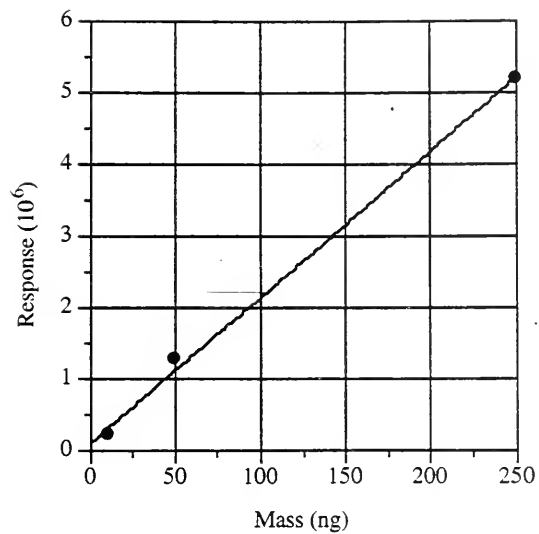
$$R^2 = 0.997$$

Massey Creek Event 2
m,p - Xylene Standard Curve



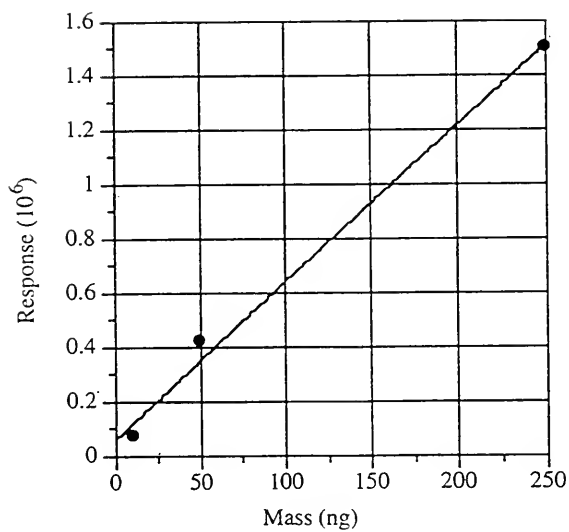
$$R^2 = 0.999$$

Massey Creek Event 2
o - Xylene Standard Curve



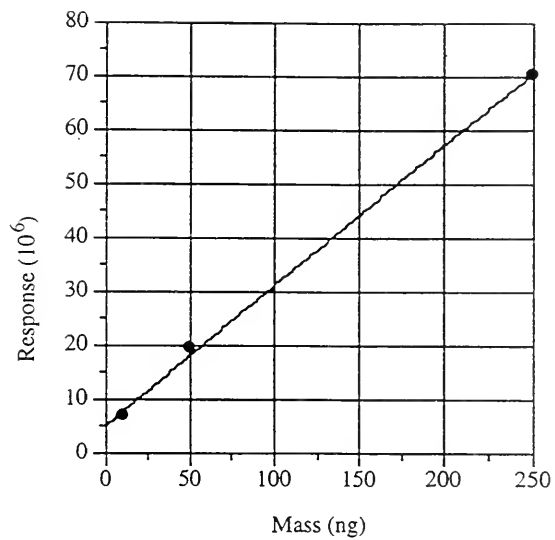
$$R^2 = 0.997$$

Massey Creek Event 2
Tetrachloroethene Standard Curve



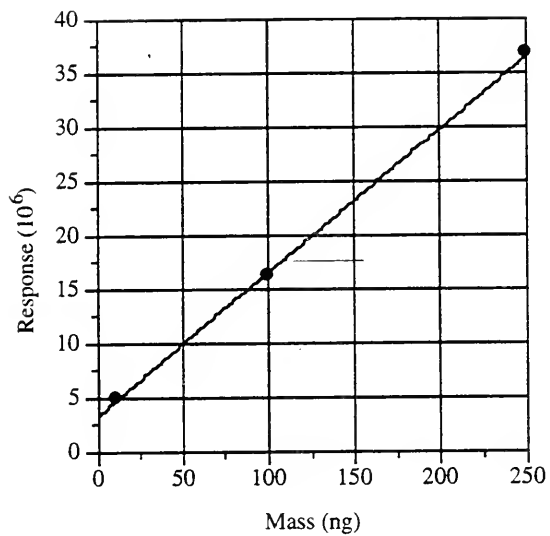
$$R^2 = 0.993$$

Massey Creek Event 3
Toluene Standard Curve



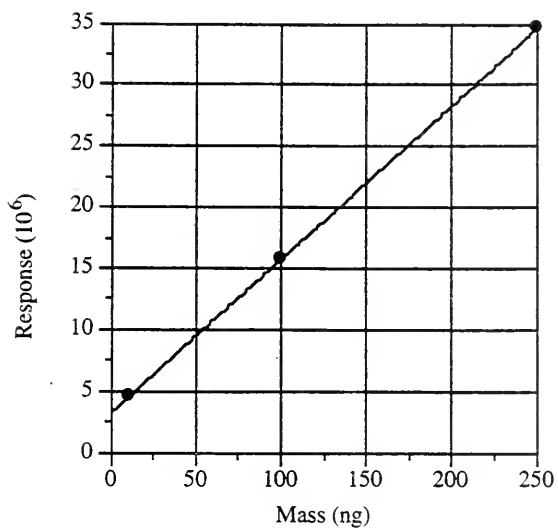
$$R^2 = 0.999$$

Massey Creek Event 3
Ethylbenzene Standard Curve



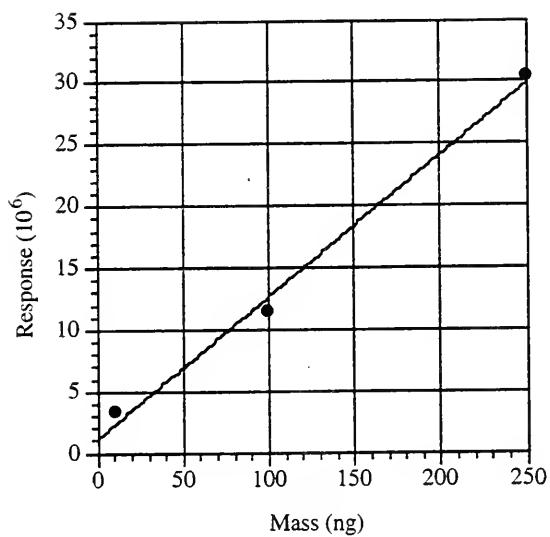
$R^2 = 0.999$

Massey Creek Event 3
m,p - Xylene Standard Curve



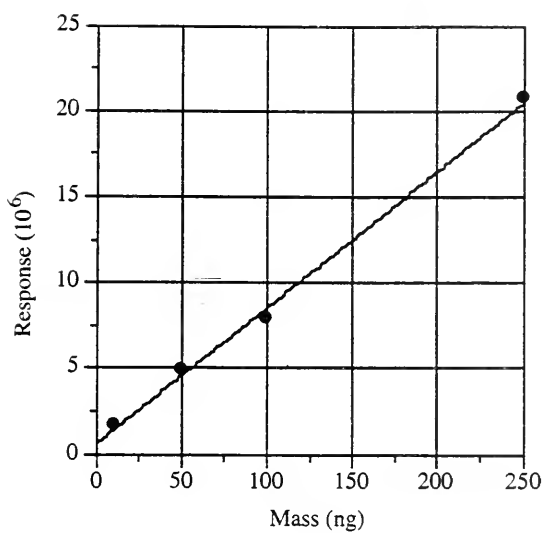
$$R^2 = 0.999$$

Massey Creek Event 3
o - Xylene Standard Curve



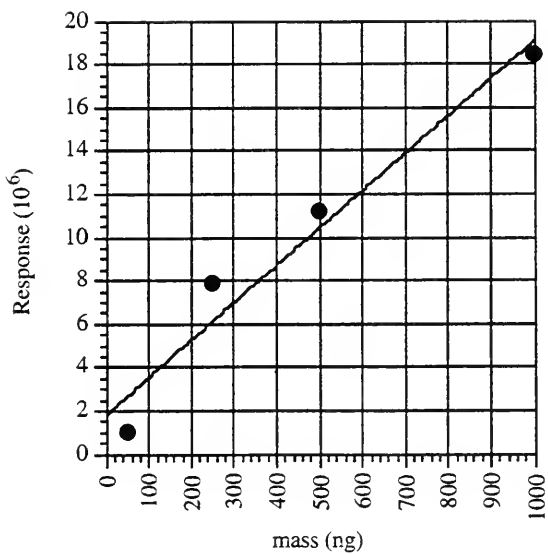
$$R^2 = 0.993$$

Massey Creek Event 3
Tetrachloroethene Standard Curve



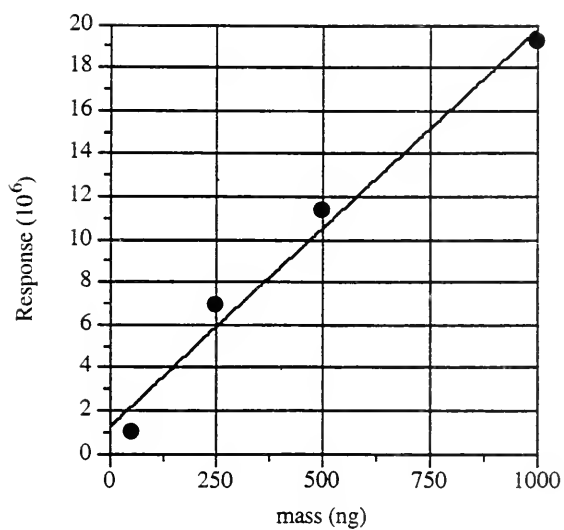
$$R^2 = 0.997$$

High Park Events 1-3
Toluene Standard Curve



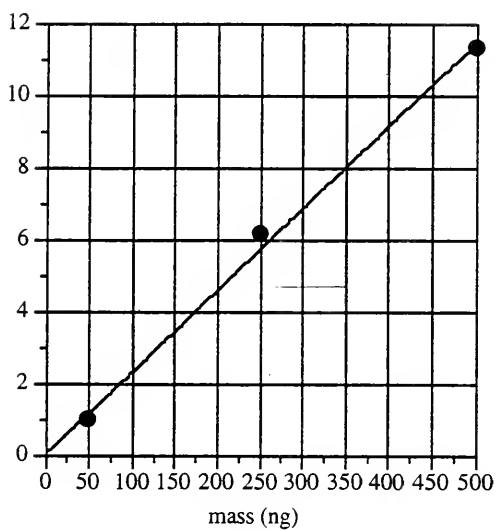
$$R^2 = 0.956$$

High Park Events 1-3
Ethylbenzene Standard Curve



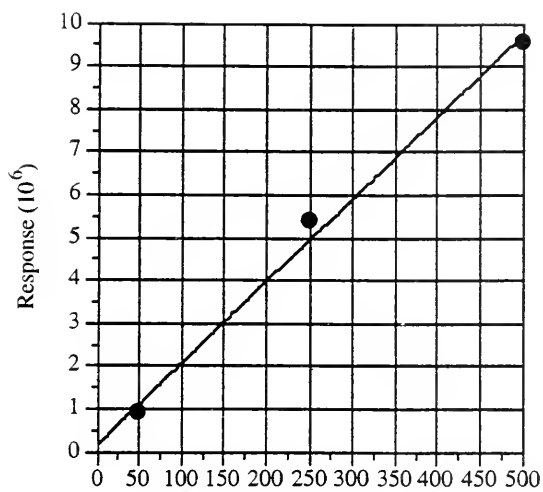
$$R^2 = 0.9810$$

High Park Events 1-3
m,p - Xylenes Standard Curve



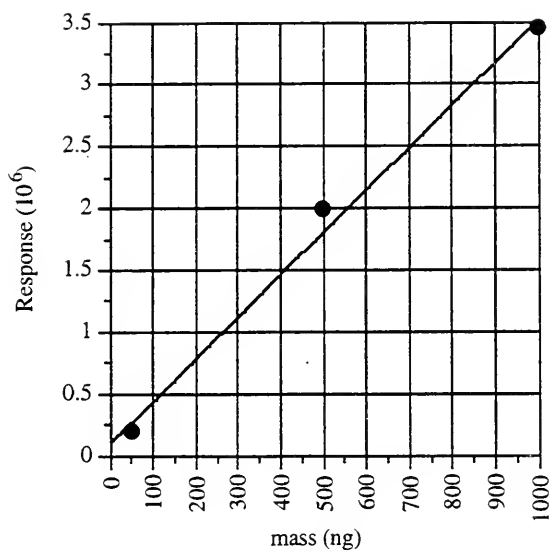
$$R^2 = 0.9964$$

High Park Events 1-3
o - Xylene standard curve



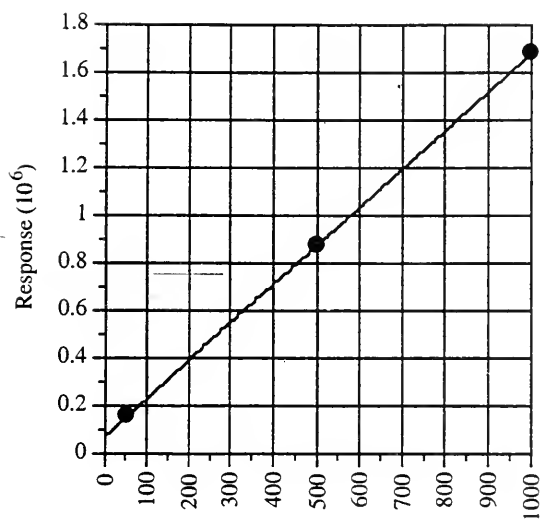
$$R^2 = 0.992$$

High Park Events 1-3
Tetrachloroethene Standard Curve



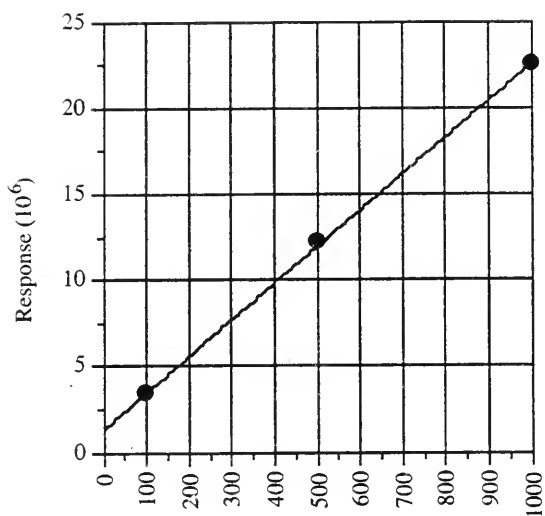
$$R^2 = 0.992$$

High Park Events 1-3
Trichloroethene Standard Curve



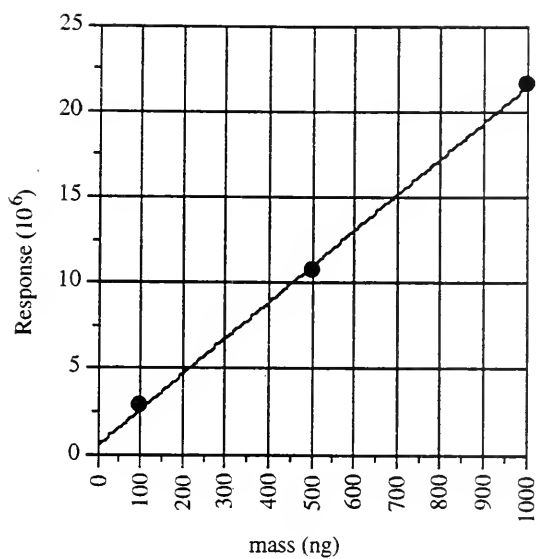
$$R^2 = 0.999$$

Massey Creek Event 5
Ethylbenzene Standard Curve



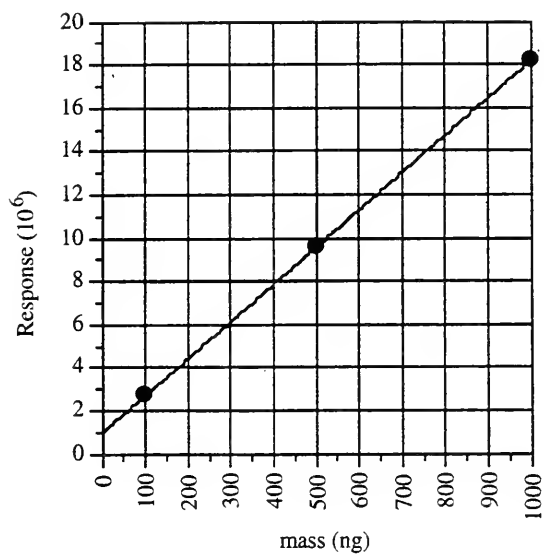
R² = 0.999

Massey Creek Event 5
m,p-Xylenes Standard Curve



$$R^2 = 0.999$$

Massey Creek Event 5
o-Xylene Standard Curve



$$R^2 = 0.999$$

APPENDIX E: MASSEY CREEK INTERCEPTOR
LIQUID SAMPLING EVENTS DATA ———

Table E.1. MCI Event 5: Gas Sampling Data.

Compound	Time	MH#	Conc. (mg/m ³)	Flowrate (m ³ /s)	Emissions (g/hr)
Ethylbenzene	15:15	7	11	0.07	2.9
		6	24	0.12	10
		5	21	0.10	7.6
		3	24	0.10	8.8
	16:00	7	10	0.07	2.6
		6	0	0.07	0
		5	3.1	0.07	0.8
		3	3.8	0.12	1.6
m,p-Xylene	15:15	7	89	0.07	22
		6	120	0.12	52
		5	104	0.10	37
		3	124	0.10	45
	16:00	7	77	0.07	19
		6	4.3	0.07	1.1
		5	16	0.07	4.0
		3	23	0.12	9.9
o-Xylene	15:15	7	18	0.07	4.5
		6	22	0.12	9.5
		5	23	0.10	8.3
		3	22	0.10	7.9
	16:00	7	17	0.07	4.3
		6	0.5	0.07	0.1
		5	5.6	0.07	1.4
		3	6.6	0.12	2.9

Table E.2. MCI Event 5: Liquid Sampling Data.

Location	Time (min)	Wastewater Concentration (µg/L)		
		Ethylbenzene	m.p - Xylenes	o-Xylene
MH9	14:15	580	2349	1576
	14:25	2426	14845	3930
	14:35	2197	6669	3627
	14:45	1351	4976	2472
	14:55	951	5206	2744
	15:05	1330	5718	3456
	15:15	2547	13170	4821
	15:25	1471	9027	4221
	15:35	1114	7645	3851
	15:45	1025	4725	2908
MH6	14:15	1213	3848	2606
	14:27	2006	9909	3236
	14:35	1461	5476	2450
	14:55	377	3361	1158
	15:05	696	3166	1466
	15:15	1014	5596	1676
	15:25	891	4029	2051
	15:36	860	6990	2339
	15:47	579	4124	1594
	15:55	461	2435	1105
	16:00	245	1758	949
MH3	14:15	962	4781	2042
	14:28	1931	8603	3615
	14:43	1508	5690	2396
	14:59	667	4961	1592
	15:20	495	4272	1435
	15:32	534	3703	1559
	15:45	975	5900	1835
	16:01	469	4288	1595

Table E.3. MCI Event 6: Liquid Sampling Data.

Compound	Composite Wastewater Concentration (µg/L)					
	MH9	MH9 dup	MH9 ave	MH6	MH6 dup	MH6 ave
Toluene	1680	1690	1685	1160	1200	1180
Tetrachloroethene	27.4	24.7	26.05	17	16.3	16.7
Ethylbenzene	86	84.9	85.45	59.9	58.2	59.1
m,p-Xylenes	425	417	421	290	282	286
o-Xylene	370	365	367.5	233	222	227.5
Cumene	77.1	73.4	75.25	51.1	49.2	50.2
Propylbenzene	398	389	393.5	245	244	244.5
3 & 4 Ethyltoluene	2270	2250	2260	1467	1500	1483.5
2 Ethyltoluene	663	634	648.5	423	416	419.5
1,3,5 Trimethylbenz	845	880.2	862.5	562	534	548
1,3 Diethylbenzene	43.3	39.3	41.3	29.7	32.6	31.2
1,4 Diethylbenzene	72.6	68.3	70.45	53.2	52.8	53

Fate of Volatile Organic Compounds in Wastewater Collection Systems

Volume III: Gas-Liquid Mass Transfer Along Sewer Reaches

Arlene Whitmore
M.Sc. thesis

Final Report

RAC Project No. 577G

Richard L. Corsi (principal investigator)

September, 1994

4. GAS-LIQUID MASS TRANSFER ALONG SEWER REACHES

4.1 BACKGROUND

Mass transfer across a gas-liquid interface is often expressed as

$$R_V = K_L \left\{ C_l - \frac{C_g}{H_c} \right\} A, \quad (4-1)$$

where,

R_V = rate of mass transfer across interface, M/T

K_L = overall mass transfer coefficient, L/T

A = interfacial area, L^2

C_l = mass concentration dissolved in liquid-phase, M/ L^3

C_g = mass concentration in gas-phase, M/ L^3

H_c = Henry's law constant, $(L^3)_{liq} / (L^3)_{gas}$.

In accordance with two-film theory (Lewis and Whitman, 1924), the overall mass transfer coefficient may be expressed as

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H_c}, \quad (4-2)$$

where,

k_l = liquid-phase mass transfer coefficient, L/T

k_g = gas-phase mass transfer coefficient, L/T.

The terms $1/k_l$ and $1/k_g H_c$ are commonly referred to as liquid and gas-phase resistances to mass transfer, respectively.

The second term on the right hand side of Equation 4-2 becomes small relative to $1/k_l$ when the product $k_g H_c \gg k_l$. For many systems k_g/k_l has been reported to be greater than 100 (Mackay and Yeun, 1983). In such cases, liquid-phase resistance represents greater than 90% of the overall resistance to mass transfer for compounds with $H_c > 0.1 \text{ L}^3_{\text{liq}} / \text{L}^3_{\text{gas}}$. However, lower values of k_g/k_l have been reported for some systems. For example, values of k_g/k_l have been reported to range from 20 to 60 (Munz and Roberts, 1989) and from 38 to 110 (Hsieh *et al.*, 1991) for mechanical surface aeration, and to be as low as 2.2 to 3.6 (Hsieh *et al.*, 1992) for diffused-bubble aeration. With k_g/k_l equal to 20, liquid-phase resistance accounts for greater than 90% of total resistance to mass transfer for compounds with $H_c > 0.5 \text{ L}^3_{\text{liq}} / \text{L}^3_{\text{gas}}$.

Of all of the variables presented in Equations 4-1 and 4-2, the mass transfer coefficients, K_L , k_l and k_g remain the most difficult to routinely quantify. As noted above, for VOCs with high H_c , concern rests primarily in obtaining a value for k_l . Although theoretical factors affecting liquid-phase mass transfer coefficients, such as surface renewal rate or hypothetical film thicknesses, have been suggested, the means to determine their effect in real systems generally does not exist. For this reason, models used to estimate gas-liquid mass transfer coefficients are empirical or semi-empirical at best, with most having been developed to predict oxygen mass transfer coefficients for clean water flowing in natural or engineered open channels (Cadwallader and McDonnell, 1969; O'Connor and Dobbins, 1958; Tsivoglou and Neal, 1976).

Parkhurst and Pomeroy (1972) developed the only reported model for mass transfer within sewer environments. According to their semi-empirical model

$$K_{Lo} = 2.67 \times 10^{-4} (1 + 0.17F^2)\gamma(US)^{3/8}, \quad (4-3)$$

where,

K_{Lo} = overall mass transfer coefficient for oxygen, m/s

F = Froude number = $\frac{U}{[gd]^{1/2}}$, -

g = gravitational acceleration = 9.8 m/s^2

- d = depth of flow, m
- γ = temperature correction factor, -
- S = slope of the energy gradient, m/m
- U = wastewater mean velocity, m/s.

For gases with high Henry's law coefficients, such as oxygen, the gas film offers relatively little resistance to mass transfer. Therefore, the overall mass transfer coefficient for oxygen is approximately equal to its liquid-phase mass transfer coefficient.

Predictions of oxygen mass transfer coefficients allow subsequent estimation of liquid-phase mass transfer coefficients for other compounds using the relationship

$$\Psi = \frac{k_{li}}{K_{Lo}} = \left\{ \frac{D_{li}}{D_{lo}} \right\}^n \quad (4-4)$$

where,

Ψ = ratio of VOC-to-oxygen liquid-phase mass transfer coefficients, -

D_{li} = liquid molecular diffusion coefficient for compound i, L^2/T

D_{lo} = liquid molecular diffusion coefficient for oxygen, L^2/T

k_{li} = liquid-phase mass transfer coefficient for compound i, L/T

K_{Lo} = overall mass transfer coefficient for oxygen, L/T

n = exponent which varies depending on the degree of liquid agitation, -

The value of n varies from 0.5 to 1.0 according to penetration (Higbie, 1935) and two-film (Lewis and Whitman, 1924) theories, respectively. Even when a value of n is not known for a given system, it has been shown that for compounds with $H_c > 0.1 \text{ L}^3_{liq} / \text{L}^3_{gas}$, Ψ generally ranges from 0.5 to 0.7 in natural surface waters and wastewater (Matter-Muller *et al.*, 1981; Smith *et al.*, 1980).

Other than Parkhurst and Pomeroy (1972), only a few researchers have investigated gas-liquid mass transfer along uniform sewer reaches. Jensen and Hvitved-Jacobsen (1991) developed a method for measuring oxygen mass transfer coefficients in a 2.3 km gravity-flow sewer reach (0.6 - 0.7 m diameter) in Aalborg, Denmark. It involved the use of krypton-85 as a gaseous radio-tracer, and tritium as a non-gaseous indicator of dispersion. A value of Ψ for krypton and oxygen had been determined in a previous study by Tsivoglou *et al.* (1965). This was coupled with Equation 4-3 to yield predicted mass transfer coefficients that were reported to be approximately 21% greater than experimentally determined transfer coefficients over three experiments.

Corsi *et al.* (1992) reported the results of four mass transfer experiments completed in two different reaches in California. Deuterated chloroform was used as a volatile tracer. Mass transfer coefficients that were predicted by combining Equations 4-3 and 4-4 were reported to be within +/- 33% of experimentally determined mass transfer coefficients.

4.2 EXPERIMENTAL METHODOLOGY

Four field experiments were completed in two operating gravity-flow sewer reaches in the City of Guelph. Each experiment was designed to facilitate the determination of K_L using surrogate volatile tracers. Experimental K_L were then used for comparison with values predicted using Equations 4-3 and 4-4, with required model variables being consistent with conditions observed during each experiment. Pipe diameters for Guelph Experimental Reach #1 (Guelph #1) and Guelph Experimental Reach #2 (Guelph #2) were 1.2 m and 0.52 m, respectively. Channel slopes were 0.10% (Guelph #1) and 3.5% (Guelph #2). The section of each reach that was used for tracer experiments was 122 m for Guelph #1 and 64 m for Guelph #2. Wastewater that was transported along Guelph #1 represented a mix of residential, commercial and light industrial discharges. Wastewater conveyed along Guelph #2 was primarily residential. The channel slope for Guelph #2 represented an extreme condition within the City of Guelph. The experimental systems are illustrated in Figures 4.1 and 4.2. Major components of each system are described below.

Headspace Ventilation

Experimental reaches were force-ventilated using a small blower powered by a portable generator. This provided constant ventilation throughout the duration of an experiment, and also accelerated the rate at which steady-state conditions were achieved. Two different blowers were used depending on the desired ventilation rate. Wooden plates (22.5 cm diameter) were sealed around the outlets of each blower. This allowed the blowers to be interchangeably mounted on a sheet metal stack 22.5 cm in diameter and 61 cm in length. This stack provided an outer shell that could be slipped over the 22.5 cm diameter vent on a junction box (Guelph #1), or mounted on Manhole #1 (Guelph #2).

Upstream transport of forced-air was not possible on Guelph #1, as the junction box received wastewater from an inverted siphon which effectively formed a gas seal. To minimize upstream gas flow on Guelph #2, a neoprene skirt was inserted in the headspace immediately upstream of Manhole #1, allowing only a small air gap between the sewer headspace and wastewater surface. Furthermore, the blower at Manhole #1 was modified to include a section of dryer hose which formed a 90° bend immediately above the wastewater surface, i.e. blowing air in the downstream direction.

Headspace ventilation rates were confirmed by dilution of an inert tracer, sulfur hexafluoride. A 40 L Tedlar® bag was filled with SF₆ (99.8% purity) and transported to the field. An air sample pump (SKC model 224-PCXR7), single-port manifold and 6.5 mm o.d. polyethylene tubing were used to inject SF₆ into the headspace of the sewer reach, approximately 6 cm above the surface of the wastewater at Manhole #1. The system was allowed to reach steady state by waiting a minimum of three aerodynamic residence times prior to collecting samples. An air sample pump and 6.5 mm o.d. polyethylene tubing were then used to draw headspace gas, at a rate of 2.5 L per minute at Manhole #2. A plastic T-connection within the line allowed the collection of five gas samples using sterile 10 mL plastic surgical syringes with PVC Luer-lok stopcocks.

Analyses of gaseous SF₆ samples were completed using a gas chromatograph (Hewlett-Packard 5890 Series II with a J & W Scientific #123-5033 30 m DB-5 capillary column) equipped with an electron capture detector (GC/ECD). All gas samples were analyzed by drawing 10 mL of air from each sample syringe followed by direct injection into the GC column. Three-point calibration curves were developed by direct-injection of standards prepared by sequential dilution of a gaseous SF₆ stock standard mixed with ultra-high purity (UHP) nitrogen. Sulfur hexafluoride concentrations in all gaseous field samples fell within the range defined by calibration curves, 0.33 to 0.66 mg/L.

Wastewater Flow Characteristics

The dilution of an inert tracer dye was selected as a practical means of determining sewer reach hydrodynamics and wastewater flow rates. Before beginning each experiment, two wastewater blanks were collected. During the hydrodynamic portion of the test, rhodamine dye (10.3 g/L) was pumped directly into wastewater below Manhole #1 at a rate of 180 mL/min for 2 minutes. Forty wastewater samples were then collected at Manhole #2. During each experiment, the sewer channel approached ideal plug-flow behavior with little axial dispersion.

A second batch of rhodamine dye (5.2 g/L) was pumped into the wastewater below Manhole #1 at a rate of 50 mL/min for 30 minutes to determine wastewater flow rate by dilution. Again, samples were collected at Manhole #2. Polyethylene tubing (6.5 mm o.d.) and a peristaltic pump (Cole-Parmer 6-600 rpm) were used for both injection and collection.

A spectrofluorometer (Turner Model 430) was used to complete rhodamine dye analyses. Four-point linear calibration curves were developed by sequential dilution of a 10 mg/L stock rhodamine dye standard and wastewater blanks collected at the beginning of each experiment were used to judge the baseline fluorescence of wastewater prior to the addition of rhodamine dye. Rhodamine dye concentrations in all liquid field samples fell within the range defined by calibration curves, 21 to 515 mg/L.

Wastewater and Headspace Fluid Characteristics

Wastewater and headspace temperatures and dissolved oxygen concentrations were measured directly using an on-line temperature / dissolved oxygen probe (YSI model # 5740) and meter (YSI model # 58) at Manhole #3 (Guelph #1) or Manhole #2 (Guelph #2). Over all experiments, wastewater temperature varied from 16 °C to 19 °C, sewer gas temperature varied from 18 °C to 23 °C, and wastewater dissolved oxygen concentrations varied from 0.2 mg/L to 4.7 mg/L.

Wastewater samples were collected at Manhole #3 (Guelph #1) or Manhole #2 (Guelph #2) using either a "dipping" cup or peristaltic pump, respectively. Those samples were used to quantify wastewater conductivity and pH in the field using portable meters (conductivity - Hanna Instruments HI # 8033; pH - Cole Parmer Chem Cadet model #5850-00). Wastewater samples were also returned to the laboratory for analysis of total suspended solids (TSS) using Standard Method 2540 D (Standard Methods, 1989). Over all experiments, the conductivity of wastewater varied from 1460 to 1580 micromhos, pH varied from 7.8 to 9.3, and TSS varied from 98 mg/L to 293 mg/L.

Volatile Tracers

Two volatile organic compounds, deuterated chloroform (CDCl_3 , 99.8% atom D) and 1,1,1-trichloroethane (TCA, 96.5%), were used as tracers during each field experiment. These compounds were selected as tracers on the basis of differences in their Henry's law coefficients, ability to dissolve to high concentrations in water prior to injection into wastewater, lack of detection in background samples collected in the experimental reaches during preliminary site investigations, and relatively low octanol-water partition coefficients (K_{ow}) and associated low affinities for adsorption to suspended solids. The latter is particularly true for the range of TSS concentrations observed over all four field experiments, as described above. The use of dual tracers, as opposed to the single compound experiments reported previously (Corsi *et al.*, 1992; Jensen and Hvitved-Jacobsen, 1991; Tsivoglou *et al.*, 1965), also allowed for

confirmation of experimental mass transfer coefficients. The physicochemical properties of each tracer are listed in Table 4.1.

In preparing for each experiment, a 40 L Tedlar® bag was filled with 23.8 L of tap water using a peristaltic pump and 6.5 mm o.d. polyethylene tubing. A 200 mL methanol solution containing the selected tracers was then pumped into the bag using a peristaltic pump and FEP Teflon® tubing. Twelve hours were allowed between bag filling and experiments in order to ensure that complete dissolution of both tracer compounds had taken place. Consideration of all experimental factors meant that different solution concentrations and/or injection rates were employed for each experiment. Over the course of the four experiments, target solution concentrations ranged from 312 to 625 mg/L for deuterated chloroform and from 279 to 558 mg/L for 1,1,1-trichloroethane.

During each experiment, the tracer solution was pumped from the Tedlar® bag into wastewater at Manhole #1 using 6.5 mm o.d. FEP Teflon® tubing and a peristaltic pump calibrated to deliver a specific flow rate dependent upon experimental conditions. The Tedlar® bag collapsed as it was evacuated, ensuring that no headspace developed during the injection period.

A minimum of three hydraulic and aerodynamic residence times were allowed prior to sample collection in order to assure steady-state conditions. Subsequent observations verified that neither gas or liquid sample concentrations increased during the course of experimental sampling. Once this time had been reached in the field, both gas and liquid samples were collected at Manhole #2. Wastewater was pumped to the surface using 6.5 mm o.d. FEP Teflon® tubing and a peristaltic pump. Four liquid samples were collected in 40 mL amber/borosilicate vials capped with 3 mm Teflon® fluorocarbon resin silicone septa (Precleaned to EPA Protocol B Cleaning Standards). Collection was accomplished with as little agitation as possible and no headspace was permitted in the capped vials. All liquid samples were immediately stored in an ice chest.

Sewer gas was pumped to the surface using 6.5 mm o.d. FEP Teflon® tubing and an air sample pump equipped with a single port manifold. Five gas samples were collected on 6.5 mm o.d. stainless steel sorbent tubes (Carbotrap™ 300 multi-bed thermal desorption tubes) sequentially packed with two

graphitized carbon black adsorbent beds (Carbotrap C and Carbotrap), and a spherical carbon molecular sieve (Carbosieve™). Twelve hours prior to each experiment, all tubes were thermally conditioned at 280 °C for 3 hours. Following gas collection, each tube was sealed using Teflon® ferrules and stainless steel Swagelok® plugs at both ends. All gas samples were immediately stored in a hermetically-sealed glass container and kept in an ice chest. Upon return to the laboratory, VOC samples were transferred to a refrigerator and maintained at 4 °C.

Prior to sample analysis, each liquid sample was concentrated onto a clean Carbotrap™ 300 adsorbent tube by sparging with charcoal-polished UHP nitrogen gas at 100 mL/min for 10 minutes. All concentrated liquid and gas samples were analyzed using the following method: thermal desorption by replacement of the internal focussing trap of a Tekmar LSC 2000 purge and trap unit (dry purge for 2.50 minutes with charcoal-polished UHP helium, desorption at 190 °C for 2.75 minutes, bake at 260 °C for 2.00 minutes); transfer to a Hewlett-Packard 5890 Series II GC oven equipped with a J & W Scientific DB-5 30 m x 0.20 mm i.d. capillary column with 1.0 µm film thickness (desorbed analytes condensed at the column head at 25 °C, oven ramp at 30 °C/min to 39 °C, hold for 2.20 minutes, ramp at 9 °C/min to 150 °C, ramp at 30 °C/min to 210 °C, hold for 2.00 minutes); transfer to a Hewlett-Packard model 5971 mass selective detector (MS) set to scan all ions from m/e 25 to m/e 250 at approximately 2 cycles/s. External calibration curves were generated using a stock solution of CDCl₃ and TCA. A minimum of four-point external calibration curves were prepared for each experiment. All experimental samples fell within the mass range defined by calibration curves, generally 40 to 800 ng.

Determination of Mass Transfer Coefficients

Overall mass transfer coefficients were determined by solving Equation 4-1 for K_L such that

$$K_L = \frac{R_v}{\left\{ C_l - \frac{C_g}{H_c} \right\} A} \quad (4-5)$$

For short reaches of sewer, e.g., reach lengths used in this study, the reduction in concentration of a VOC dissolved in wastewater is generally much less than analytical (GC/MS) accuracy. However, for steady-state conditions the accumulation of volatile tracers in the headspace of the experimental systems was sufficient to easily quantify gas-phase concentrations. Thus, integrated emissions along the experimental reaches were determined by

$$R_v = Q_g C_g \quad (4-6)$$

where,

R_v = net rate of mass transfer across gas-liquid interface, M/T

Q_g = gas flow rate in sewer headspace, L³/T

C_g = tracer concentration in gas phase at Manhole #2, M/L³.

The concentration in wastewater (C_l , M/L³) was measured from liquid samples collected at Manhole #2 in each reach. Henry's law coefficients for CCl₃ and TCA were estimated using wastewater temperatures according to Gossett (1987). No perturbations of interfacial surface area were observed during any of the four field experiments. Thus, surface area (A) was determined as the product of reach length and surface width, where surface width was estimated by geometric considerations using pipe diameter and depth of flow. For the four experiments described in this paper, surface width varied from 0.33 m (Guelph #2) to 1.0 m (Guelph #1), and surface area varied from 21 m² (Guelph #2) to 127 m² (Guelph #1).

The gas concentration required to determine the C_g/H_c term in Equation 4-5 varied as a function of distance along each sewer reach. However, C_g/H_c was generally much less than C_l . For example, the magnitude of C_g/H_c for CCl₃ was less than 25% of C_l for all experiments. Similarly, for TCA the magnitude of C_g/H_c was always less than 5% of C_l . Thus, an average value of C_g was used, i.e., 50% of the maximum value at the end of the reach. Based on the analyses described above, this approximation was determined to yield less than a 2% difference relative to values of K_L determined with either a maximum or minimum estimate of C_g for TCA. Similarly, the difference for

CDCl₃ should not have been greater than 12% relative to values of K_L determined with either a maximum or minimum estimate of C_g.

The approach described above was verified using a two-phase finite volume model described elsewhere (Corsi *et al.*, 1992). Model inputs were consistent with conditions for each of the four experiments. Differences between iteratively back-calculated K_L values obtained using the model and those determined using Equations 4-5 and 4-6 were always less than 7%, well within the experimental uncertainties described below.

Error Estimation

Errors associated with determination of experimental K_L for this study were estimated using an error propagation method based on differentiation of Equations 4-5 and 4-6 with respect to each variable on the right-hand-side of Equation 4-5:

$$\Delta K_L = \sum \frac{\partial K_L}{\partial X_i} \Delta X_i \quad (4-7)$$

where,

ΔK_L = overall uncertainty in K_L, M/T

X_i = variable i

ΔX_i = uncertainty in variable i

Percent uncertainties associated with Q_v, C_g and C_l were assumed to be equal to the maximum coefficients of variation for each variable over all four experiments. Uncertainties in H_c were assumed to be +/- 15% based on maximum differences reported in the literature for consistent temperatures. An uncertainty of 20% for A was based on maximum coefficients of variation in replicate rhodamine dye samples which were used to determine wastewater flow rates. The signs associated with ΔX_i were selected to maximize estimates of uncertainty, i.e. error estimates for K_L were determined as worst-case.

Sufficient data were not available to estimate uncertainties in mass transfer coefficients determined from previous studies in Denmark (Jensen and Hvitved-Jacobsen, 1991) and California (Corsi *et al.*, 1992).

4.3 RESULTS AND DISCUSSION

Table 4.2 provides a summary of wastewater and gas flow conditions for Guelph #1 (Experiments 1.1 - 1.3) and Guelph #2 (Experiment 2.1). The gas flow rates listed in Table 4.2 may be translated into ventilation rates expressed as number of turnovers per day (TuPD). By convention, these turnovers are based on empty pipe volume. Ventilation rates for Experiments 1.1 through 2.1 varied from 22 to 190 TuPD. These ventilation rates were one to two orders of magnitude higher than estimates of natural ventilation rates reported by Pescod and Price (1982). They reported that ventilation rates required to maintain the 85% of normal oxygen levels typical in 1.50 m and 0.45 m diameter sewer pipe atmospheres ranged from 0.51 to 2.34 TuPD, respectively. However, Quigley *et al.* (1993) reported measured ventilation rates of as high as 19 TuPD in a municipal sewer interceptor in Toronto, Ontario (see Chapter 3).

Average gas and liquid-phase concentrations of each volatile tracer are also presented in Table 4.2. In the case of gas samples, a time-weighted average (TWA) was used to reflect different lengths of time over which gas samples were collected. Overall, liquid samples exhibited lower variances than gas samples. Coefficients of variation for liquid samples ranged from 1.7% to 24%, while coefficients of variation for gas samples ranged from 8.9% to 43%.

Sewer operating characteristics are listed in Table 4.3 for the Guelph experiments as well as experiments completed by Corsi *et al.* (1992) and Jensen and Hvitved-Jacobsen (1991). The pipe diameter, slope, wastewater flow rates, and gas flow rates associated with Guelph #1 fell within the range defined by the two California reaches studied by Corsi *et al.* (1992). Guelph #2, however, was significantly different than the other reaches in terms of its large channel slope and wastewater velocity, with corresponding high degree of turbulent mixing of the wastewater.

Experimental Mass Transfer Coefficients

Experimental mass transfer coefficients (K_L) are listed in Table 4.4 for the four experiments described in this paper, along with those reported for Davis, Sacramento, and Aalborg (Corsi *et al.*, 1992; Jensen and Hvitved-Jacobsen, 1991). Uncertainty estimates for the experiments described in this paper are also provided in Table 4.4. Experimentally determined K_L were generally estimated to be accurate to within a factor of two. Insufficient information was available to estimate uncertainties for the California and Aalborg experiments. Additionally, for the Aalborg experiments there was insufficient data provided to estimate K_L . Thus, only the K_{LA} values reported by the authors are listed in Table 4.4.

Over all experiments, mass transfer coefficients varied by a factor of 11, from a low of 0.014 m/hr (Guelph #1; TCA - Expt. 1.2) to a high of 0.15 m/hr (Guelph #2; TCA). Mass transfer coefficients generally increased in the order of Guelph #1, Sacramento, Davis and Guelph #2. The latter should approach a maximum for municipal sewers, as Guelph #2 was characterized by both a large channel slope (3.5%) and high wastewater mean velocity (1.5 m/s). These results suggest that K_L can vary significantly from reach-to-reach, and that application of reach-independent mass transfer coefficients to predict gas-liquid mass transfer of VOCs in sewers may lead to significant error.

For the two Guelph reaches, there were no apparent differences in K_L between $CDCl_3$ and TCA. For two of the experiments (Expt. 1.1 and Expt. 2.1) K_L values for $CDCl_3$ and TCA were essentially equivalent. Values of K_L for $CDCl_3$ were approximately factors of 2.0 greater and less than K_L for TCA during Experiments 1.2 and 1.3, respectively. For the experimental conditions, values of H_c for TCA were approximately a factor of five greater than H_c for $CDCl_3$. Therefore, if k_g is not much greater than k_l in Equation 4-2, K_L for $CDCl_3$ should have been observed to be lower than K_L for TCA. Since this did not appear to be the case, it is likely that k_g was much greater than k_l and gas-phase resistance to mass transfer was small for the four Guelph experiments.

The results listed in Table 4.4 suggest that the experimental protocol outlined in this paper should allow determination of reach-specific mass transfer coefficients to within a factor of two or better. Furthermore, the use of

dual tracers should prove valuable for confirmation of VOC mass transfer coefficients or the determination of both liquid and gas-phase mass transfer coefficients. The latter would require one volatile tracer, e.g., $H_c > 0.1 \text{ L}^3_{\text{liq}} / \text{L}^3_{\text{gas}}$, for which gas-phase resistance to mass transfer is small, and one tracer with a relatively low value of H_c , e.g., $<< 0.1 \text{ L}^3_{\text{liq}} / \text{L}^3_{\text{gas}}$, for which gas-phase resistance to mass transfer is significant.

Effects of Potential Energy Dissipation

As noted above, overall mass transfer coefficients generally increased in the order of Guelph #1, Sacramento, Davis and Guelph #2. This was also the order of increasing US , where U is wastewater mean velocity and S is the slope of the energy gradient. The value of S is equal to channel slope for uniform flow conditions. Conceptually, US is the rate of potential energy dissipation of a liquid flowing in an open channel. The rate of potential energy dissipation should be proportional to production of turbulent kinetic energy and associated turbulent mixing within the liquid stream. According to penetration theory (Higbie, 1935), the mass transfer coefficient of a compound should be directly proportional to the degree of turbulent mixing as measured by surface renewal rate.

To estimate K_{Lo} for oxygen in natural streams, several models have been developed of the form

$$K_{Lo} = b(US)^m \quad (4-8)$$

where

b = empirical constant, -

m = empirical or semi-empirical power constant, -

Several models of the form described by Equation 4-8 were reviewed by Frexes *et al.* (1984). They noted that values of m obtained by various investigators were in the range of 0.375 to 1, with most approximately 0.5. The lower-bound

of this range is consistent with Equation 4-3. A relationship similar to Equation 4-8 can be used to model K_L for VOCs.

Taking \log_{10} of each side of Equation 4-8 applied to VOCs yields

$$\log_{10}(K_L) = m\log_{10}(US) + \log_{10}(b) \quad (4-9)$$

or

$$-\log_{10}(K_L) = -m\log_{10}(US) - \log_{10}(b) \quad (4-10)$$

Thus, a plot of $-\log_{10}(K_L)$ versus $-\log_{10}(US)$ should allow an estimation of m and b through linear best-fit analysis.

As K_L is a function of temperature [$K_L(T)$], analyses of experimental data should account for differences in liquid temperature between experiments. This is typically done by adjusting experimental $K_L(T)$ to a reference temperature, say 20 °C [$K_L(20)$], using an empirical adjustment factor θ such that

$$K_L(20) = \frac{K_L(T)}{\theta^{T-20}} \quad (4-11)$$

The value of θ is commonly accepted, as an ASCE standard, to be 1.024 for oxygen (ASCE, 1984). However, this value has also been applied to adjust mass transfer coefficients for other volatile chemicals such as krypton (Jensen and Hvitved-Jacobsen, 1991). For this study, uncertainties associated with extrapolating $\theta = 1.024$ to chemicals other than oxygen were small, as wastewater temperatures were close to 20 °C (16 - 19°C) over all four field experiments.

Values of b and m were obtained for the combined data set associated with Guelph #1, Guelph #2, Sacramento and Davis using Equations 4-10 and 4-11. A plot of $-\log_{10}[K_L(20)]$ versus $-\log_{10}(US)$ for the combined data set is provided in Figure 4.3. The data exhibited a clear trend of increasing K_L with increasing rate of potential energy dissipation. A least-squares best-fit equation using all data lead to values of $m = 0.40$ and $b = 0.52$. The resulting R^2 was 0.86. The power constant m was within the range of values reported previously for

oxygen transfer to natural streams, and was close to the value used in Equation 4-3.

The predicted b value (b_{pred}) using Equation 4-3, converted to units of m/h , and Equation 4-4 is

$$b_{\text{pred}} = 0.96\Psi(1 + 0.17F^2). \quad (4-12)$$

The term $(1 + 0.17F^2)$ is intended to account for increases in surface area due to surface disturbances as Froude number (F) increases. For the four Guelph experiments, F ranged from 0.48 to 0.49 for Guelph #1, and was equal to 2.3 for Guelph #2. The associated values of $(1 + 0.17F^2)$ were 1.039 to 1.041 for Guelph #1, and 1.89 for Guelph #2. Use of $n = 1.0$ and $n = 0.5$ in Equation 4-4 lead to Ψ estimates of 0.48 and 0.69, respectively, for CDCl_3 . Similarly, Ψ estimates were 0.43 and 0.65 for TCA. Thus, for Guelph #1, b_{pred} ranged from 0.48 to 0.69 for CDCl_3 and from 0.43 to 0.65 for TCA. The experimental b of 0.52 was well within each of these ranges. For Guelph #2, b_{pred} ranged from 0.87 to 1.25 for CDCl_3 , and from 0.78 to 1.18 for TCA. Thus, b_{pred} was greater than the best-fit experimental b by 34% to 127%. This was due to the large Froude number for Experiment 2.1, and subsequent increase in predicted surface area. However, as noted previously, visual observations during Experiment 2.1 (Guelph #2) suggested that surface disturbances were negligible at both Manhole #1 and Manhole #2.

Comparison with Predicted Mass Transfer Coefficients

Liquid-phase mass transfer coefficients (k_l) were estimated using Equations 4-3 and 4-4, such that

$$k_l = 2.67 \times 10^{-4} \left\{ \frac{D_{li}}{D_{lo}} \right\}^n (1 + 0.17F^2) \gamma (\text{US})^{3/8}. \quad (4-13)$$

Associated ranges of mass transfer coefficients predicted using $n = 0.5$ and $n = 1.0$ are listed in Table 4.4.

As noted previously, use of Equation 4-3 with $\Psi = 0.83$ for krypton lead to a slightly lower k_{la} than the average K_{La} observed experimentally for

Aalborg experiments. For Davis and Sacramento experiments, there was no apparent trend in differences between experimental K_L and predicted k_l . Two of the four experiments (Davis Test 3 and Sacramento) lead to K_L that were encompassed by corresponding ranges of k_l . Experimental K_L for Davis Tests 1 and 2 were 21% lower than the predicted lower-bound k_l and 3% greater than the predicted upper-bound k_l , respectively. It is likely that these differences were well within experimental error.

For the two Guelph sewer reaches, experimental K_L were less than predicted lower-bound k_l for six of eight experiments. On average, the ratio of K_L (experimental) to k_l (predicted lower-bound) was 0.81, and the ratio of K_L (experimental) to k_l (predicted upper-bound) was 0.55 over all eight experiments. Omitting Guelph #2, the ratio of K_L (experimental) to k_l (predicted lower-bound) was 0.92, and the ratio of K_L (experimental) to k_l (predicted upper-bound) was 0.62. As described above, these differences can not be readily explained by gas-phase resistance to mass transfer. However, differences between K_L (experimental) and k_l (predicted upper-bound) were generally within estimated experimental uncertainty for Guelph #1, and differences between K_L (experimental) and k_l (predicted lower-bound) were within experimental uncertainties for Guelph #2. The most significant differences between K_L (experimental) and k_l (predicted) occurred for Guelph #2, in which case K_L (experimental) for both CDCl_3 and TCA were approximately a factor of two less than lower-bound k_l and three less than upper-bound k_l .

Based on the results of experiments completed on five sewer reaches, Equations 4-3 and 4-4 provide reasonable first-estimates of K_L for VOCs in sewers, providing that gas-phase resistance to mass transfer is small ($k_g H_c \gg k_l$). Equations 4-3 and 4-4 appear to be less reliable for sewers with steep channel slopes, i.e., characterized by rapid dissipation of potential energy and associated production of turbulent mixing. For such conditions, the data reported in this study indicate that Equations 4-3 and 4-4 may overestimate K_L by a factor of two or three. Depending on the specific application, this may warrant the experimental determination of reach-specific K_L using volatile tracers.

Stripping of VOCs along Sewer Reaches

Ultimately, knowledge of VOC mass transfer coefficients along sewer reaches can be used to estimate concentration reductions in wastewater as well as mass emission rates. Assuming that gas-liquid mass transfer is the dominant fate mechanism for VOCs in sewers, plug-flow conditions exist in both the gas and liquid phases, and sewer ventilation is uniformly distributed along a reach, the following two mass balance equations can be used to predict gas and liquid-phase VOC concentrations along the reach:

$$\frac{\partial C_g}{\partial t} = - \frac{\partial U_g C_g}{\partial x} + K_L a \left(C_l - \frac{C_g}{H_c} \right) \frac{V_l}{V_g} - \frac{Q_{v \text{ out}}}{V_g} C_g + \frac{Q_{v \text{ in}}}{V_g} C_a, \quad (4-14)$$

and

$$\frac{\partial C_l}{\partial t} = - \frac{\partial U_l C_l}{\partial x} + - K_L a \left(C_l - \frac{C_g}{H_c} \right), \quad (4-15)$$

where,

C_a = ambient concentration of VOC, M/L³

t = time, T

U_g, U_l = mean velocities in gas and liquid phases, respectively, L/T

x = spatial coordinate (or distance along sewer reach), L

a = specific surface area = A/V_l , 1/L

$Q_{v \text{ in}}, Q_{v \text{ out}}$ = gas ventilation rates in and out of control volume, L³/T

V_g, V_l = gas and liquid volumes, respectively, L³.

A simplified analytical solution can be derived given the following additional assumptions:

1. $C_g \gg C_a$,
2. steady and continuous VOC discharge, wastewater flow and gas ventilation rates,

3. steady-state solution of VOC concentration ($t \rightarrow \infty$).

Equations 4-14 and 4-15 can then be solved simultaneously to yield

$$C_1 = C_{10} \exp \left\{ \frac{-K_L a}{U_1} \left[1 - \frac{1}{G+1} \right] x \right\}, \quad (4-16)$$

$$G = \frac{Q_v H_c}{V_1 K_L a}. \quad (4-17)$$

where,

C_{10} = VOC concentration in wastewater at $x = 0$, M/L³.

The term G is a dimensionless variable which represents the effects of finite ventilation on mass transfer reduction associated with VOC accumulation in a sewer headspace.

The reach length that corresponds to 50% stripping efficiency (half-length = $x_{1/2}$) can then be solved by setting $C_1/C_{10} = 0.5$ and taking the natural logarithm of each side of Equation 4-16 such that

$$x_{1/2} = \frac{0.693 U_1 V_1}{K_L a \left[1 - \frac{1}{G+1} \right]}. \quad (4-18)$$

Values of K_L and other parameters determined for each of the four Guelph experiments were substituted into Equation 4-18. To assess the effects of ventilation magnitude on half-length, headspace ventilation rate was allowed to vary from 0.3 to 100 turnovers per day. Results are plotted in Figure 4.4.

Half-length was determined to be highly sensitive to ventilation rate for ventilation rates of less than five turnovers per day. At a ventilation rate of 0.3 turnovers per day, half-lengths ranged from 74 km for Experiment 1.1 to 34 km for Experiment 2.1. At a ventilation rate of 100 turnovers per day, half-lengths varied from 13 km for Experiment 1.1 and Experiment 1.2, to 1.0 km for Experiment 2.1. For all intents and purposes, values of half-length for experiments in Guelph #1 were constant for ventilation rates of greater than 10 turnovers per day. This suggests that an assumption of infinite ventilation is valid for Guelph #1 if the headspace ventilation rate exceeds 10 turnovers per

day. Results also indicate that at ventilation rates of less than five turnovers per day, long reach lengths would be necessary to strip 50% of 1,1,1-trichloroethane.

Half-length for Guelph #2 continued to decrease for ventilation rates greater than 100 turnovers per day. Thus, an assumption of infinite ventilation in Guelph #2 could lead to significant overestimation of VOC emissions. Nevertheless, even at ventilation rates as low as five turnovers per day, short reaches of sewer can lead to relatively high VOC stripping efficiencies given appropriate sewer operating conditions, e.g., steep channel slope and low depth of flow.

The effects of ventilation magnitude and pattern on VOC emissions from sewers have been described elsewhere (Corsi *et al.*, 1989). It has been reported that VOC stripping efficiency is far more sensitive to ventilation magnitude than to ventilation pattern. For example, assumptions of uniform ventilation, i.e., equal ventilation inflows and outflows distributed along the length of a sewer reach, and flow-through (co-current) ventilation patterns generally lead to near identical VOC stripping efficiencies. For this study, the CORAL model (Corsi *et al.*, 1992) was used in addition to Equations 4-16 and 4-18 to estimate VOC stripping efficiencies and half-lengths for co-current ventilation. In all cases, half-lengths predicted by CORAL and Equation 4-18 differed by less than 3%.

4.4 SUMMARY AND CONCLUSIONS

For the four field experiments described in this paper, values of K_L varied by an order of magnitude, from a low of 0.014 m/hr to a high of 0.15 m/hr. The latter is believed to approach an upper-bound for most sewer systems. Uncertainties in experimental K_L were estimated to be less than a factor of two.

The experimental data associated with this study were combined with those obtained from previously reported studies. The resulting set of data was compared with the rate of potential energy dissipation (US) for each

experiment. Over all experiments, a strong correlation was observed between K_L and US, with proportionality and power constants nearly equivalent to a diffusivity-adjusted oxygen transfer model published previously. Differences in values of K_L determined in the field and predicted using the aforementioned model were generally less than experimental uncertainty on an experiment-by-experiment basis.

Finally, physical conditions and K_L values determined for the experiments described in this paper were used to predict sewer half-lengths necessary to strip 50% of 1,1,1-trichloroethane. Half-lengths ranged from a low of 1.0 km for the maximum K_L and ventilation rate, to a high of greater than 70 km for the minimum K_L and ventilation rate. These results indicate the importance of appropriate determination of both K_L and ventilation magnitude for estimating VOC stripping from sewer reaches.

4.5 REFERENCES

- American Society of Civil Engineers (ASCE), "A Standard for the Measurement of Oxygen Transfer in Clean Water," Oxygen Transfer Standards Committee, New York, N.Y. (1984).
- Cadwallader, T.E., and A.J. McDonnell, "A Multivariate Analysis of Reaeration Data," *Water Research*, 3, pp. 731-742 (1969).
- Corsi, R.L., D.P.Y. Chang, and E.D. Schroeder, "Assessment of the Effects of Ventilation Rates on VOC Emissions from Sewers," *Proceedings of the WPCF/EPA Workshop on Air Toxics Emissions and POTWs*, Alexandria, Virginia (1989).
- Corsi, R.L., D.P.Y. Chang, and E.D. Schroeder, "A Modeling Approach for VOC Emissions from Sewers," *Water Environment Research*, 64, pp. 734-741 (1992).
- Frexes, P., G.H. Jirka, and W. Brutsaert, "Examination of Recent Field Data on Stream Reaeration," *Journal of Environmental Engineering, ASCE*, 110, pp. 1179-1183 (1984).

- Gossett, J.M., "Measurement of Henry's Law Constants for C₁ and C₂ Chlorinated Hydrocarbons," *Environmental Science and Technology*, **21**, pp. 202-208 (1987).
- Higbie, R., "The Rate of Exposure of a Pure Gas into a Still Liquid During Short Periods of Exposure", *Transactions, American Inst. of Chem. Engrs.*, **31**, (1935).
- Howard, P.H. (ed.), "Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Volume II. Solvents," Lewis Publishers, Inc., Chelsea, Michigan (1990).
- Hsieh, C.-C., S.R. Kyoung, and M.K. Stenstrom, "Estimating Emissions of Twenty VOCs: Surface Aeration" *Paper Presented at the 64th Annual Conference of the Water Environment Federation*, Toronto, Ontario (1991).
- Hsieh, C.-C., R.W. Babcock, and M.K. Stenstrom, "Estimating Semi-volatile Organic Compound Emission Rates and Oxygen Transfer Coefficients in Diffused Aeration" *Paper Presented at the 65th Annual Conference of the Water Environment Federation*, New Orleans, Louisiana (1992).
- Jensen, N.A., and T. Hvitved-Jacobsen, "Method of Measurement of Reaeration in Gravity Sewers using Radiotracers," *Research Journal of the Water Pollution Control Federation*, **63**, pp. 758-767 (1991).
- Lewis, W.K., and W.G. Whitman, "Principles of Gas Absorption," *Industrial and Engineering Chemistry*, **16**, pp. 1215-1220 (1924).
- Mackay, D., and T.K. Yeun, "Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water," *Environmental Science and Technology*, **17**, pp. 211-217 (1983).
- Matter-Muller, C., W. Gujer, and W. Giger, "Transfer of Volatile Substances from Water to the Atmosphere," *Water Research*, **15**, pp. 1271-1279 (1981).
- Munz, C., and P.V. Roberts, "Gas and Liquid-Phase Mass Transfer Resistances of Organic Compounds During Mechanical Surface Aeration," *Water Research*, **23**, pp. 589-601 (1989).

- O'Connor, D.J., and W.E. Dobbins, "Mechanisms of Reaeration in Natural Streams," In *Transactions, ASCE*, **123**, pp. 641-684 (1958).
- Parkhurst, J.D., and R.D. Pomeroy, "Oxygen Absorption in Streams," *Journal of the Sanitary Engineering Division, ASCE*, **98**, pp. 101-123 (1972).
- Pescod, M.B., and A.C. Price, "Major Factors in Sewer Ventilation," *Journal of the Water Pollution Control Federation*, **54**, pp. 385-397 (1982).
- Quigley, C., P. Martos, and R.L. Corsi, "VOC Emissions from a Municipal Sewer Interceptor," *Proceedings of the 86th Annual Meeting of the Air and Waste Management Association*, Denver (1993).
- Smith, J.H., D.C. Bomberger, and D.L. Haynes, "Prediction of the Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies," *Environmental Science and Technology*, **14**, pp. 1332-1337 (1980).
- "Standard Methods for the Examination of Water and Wastewater," 17th Ed., L.S. Clesceri, A.E. Greenberg, and R.R. Trussell, eds., American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington D.C. (1989).
- Tsivoglou, E.C., R.L. O'Connell, C.M. Walter, P.J. Godsil, and G.S. Logsdon, "Tracer Measurements of Atmospheric Reaeration I. Laboratory Studies," *Journal of the Water Pollution Control Federation*, **37**, pp. 1343-1362 (1965).
- Tsivoglou, E.C., and L.A. Neal, "Tracer Measurements of Reaeration II. Predicting the Reaeration Capacity of Inland Streams," *Journal of the Water Pollution Control Federation*, **48**, pp. 2669-2689 (1976).

Table 4.1 Physicochemical properties of tracers used in mass transfer experiments

Compound	Molecular Weight	Solubility @ 25 °C, mg/L	Log ₁₀ (K _{ow})	H _c @ 20 °C (mg/L)-gas / (mg/L)-liq
CDCl ₃	120.4	7950	1.97	0.12
TCA	133.4	1495	2.49	0.60

Log₁₀(K_{ow}) from Howard (ed.) (1990); H_c based on Gossett (1987).

Table 4.2 Flow conditions and tracer concentrations for mass transfer experiments

Experiment	Wastewater		Sewer Gas		Concentration (mg/m ³)			
	Flow Rate m ³ /s	Velocity m/s	Flow Rate m ³ /min	Velocity m/s	CDCl ₃		TCA	
					liquid	gas	liquid	gas
1.1	0.17	0.72	2.5	0.044	18	0.38	8.4	0.20
1.2	0.071	0.56	2.1	0.035	13	0.25	5.0	0.06
1.3	0.10	0.62	11	0.18	49	0.15	42	0.23
2.1	0.020	1.5	1.8	0.15	94	2.3	99	2.8

Table 4.3 Sewer operating conditions for mass transfer experiments

Characteristic	Guelph #1	Guelph #2	Aalborg ^a	Davis ^b	Sacramento ^b
Diameter, m	1.2	0.52	0.6-0.7	0.5	2.6
Slope, %	0.10	3.5	0.09	0.24	0.063
Wastewater Flow, m ³ /s	0.071-0.17	0.020	0.018-0.021	0.03-0.06	2.1-2.6
Gas Flow, m ³ /s	0.035-0.18	0.030	c	0.02-0.03	1.8
Length, m	122	64	2310	131	291

a. from Jensen and Hvitved-Jacobsen (1991).

b. from Corst *et al.* (1992).

c. The Aalborg reach was not force-ventilated, and natural ventilation rates were not reported.

Table 4.4 Experimental and predicted mass transfer coefficients

Site	Compound	Mass Transfer Coefficient, m/h		Expt. Uncertainty (factor of)
		Experimental	Predicted	
<i>Guelph #1</i>				
Expt 1.1	CDCl ₃	0.027	0.029 - 0.041	2.2
	TCA	0.029	0.026 - 0.039	2.1
Expt 1.2	CDCl ₃	0.024	0.027 - 0.039	2.3
	TCA	0.014	0.023 - 0.035	2.0
Expt 1.3	CDCl ₃	0.018	0.028 - 0.040	2.1
	TCA	0.032	0.025 - 0.038	2.1
<i>Guelph #2</i>				
Expt 2.1	CDCl ₃	0.14	0.29 - 0.42	2.1
	TCA	0.15	0.28 - 0.42	2.0
<i>Davis</i>				
Test 1	CDCl ₃	0.039	0.049 - 0.069	NA
Test 2	CDCl ₃	0.071	0.049 - 0.069	NA
Test 3	CDCl ₃	0.048	0.040 - 0.058	NA
<i>Sacramento</i>				
	CDCl ₃	0.041	0.036 - 0.052	NA
<i>Aalborg</i>				
	Krypton	0.42/h ^a	0.36/h ^a	NA

a. Aalborg transfer coefficients reported as $K_L a$ ($a = A/V$); A = total surface area and V = total system volume. Flow data were not provided to allow calculation of K_L .
 NA. Insufficient data available to estimate experimental uncertainties in K_L .

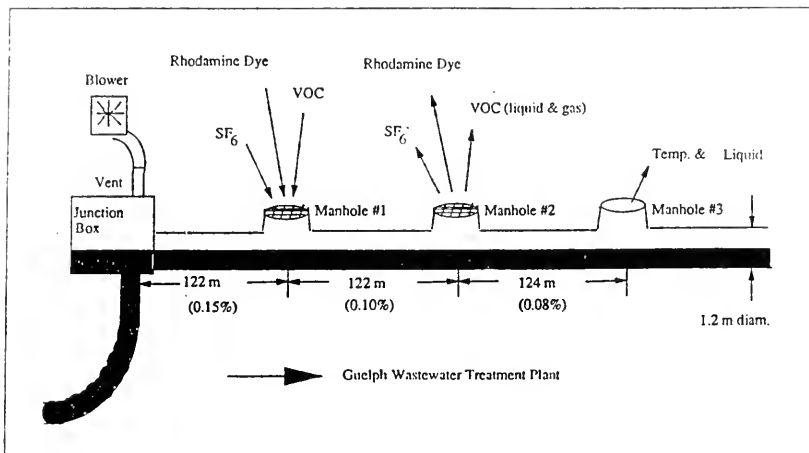


Figure 4.1 Experimental system to determine mass transfer coefficients (Guelph #1)

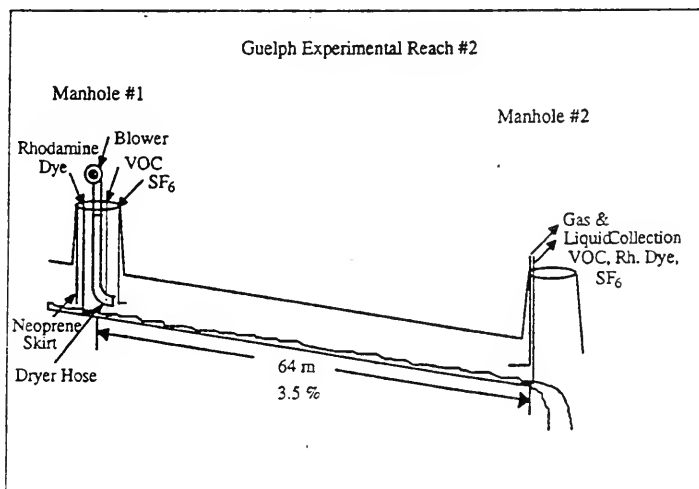


Figure 4.2 Experimental system to determine mass transfer coefficients (Guelph #2)

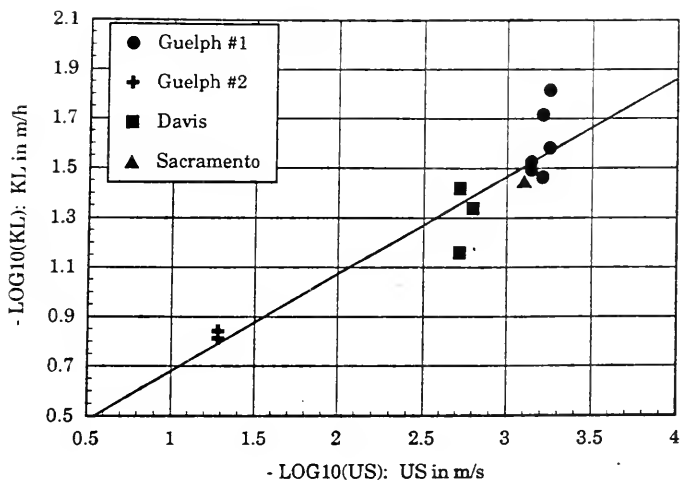


Figure 4.3 Relationship between potential energy dissipation and mass transfer coefficients

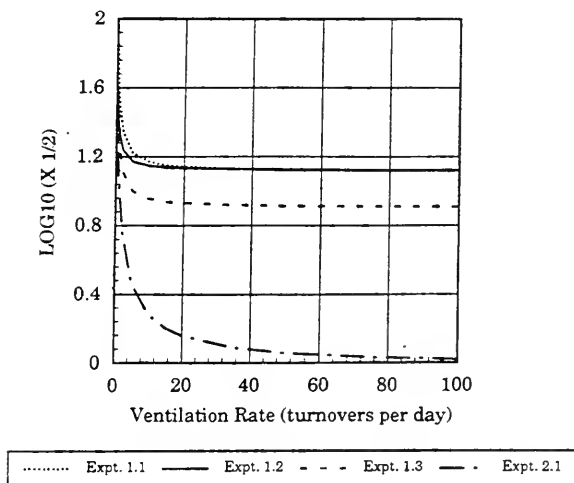


Figure 4.4 Predicted sewer half-lengths for 1,1,1-trichloroethane

GAS-LIQUID MASS TRANSFER OF VOLATILE ORGANIC COMPOUNDS
ALONG UNIFORM SEWER REACHES

A Thesis
Presented to
The Faculty of Graduate Studies
of
The University of Guelph

by
ARLENE WHITMORE

In partial fulfilment of requirements
for the degree of
Master of Science
January, 1993.

ABSTRACT

GAS-LIQUID MASS TRANSFER OF VOLATILE ORGANIC COMPOUNDS ALONG UNIFORM SEWER REACHES

Arlene Whitmore
University of Guelph, 1993

Advisor:
Professor R. L. Corsi

The research presented in this thesis focused on gas-liquid mass transfer of volatile organic compounds (VOCs) along uniform sewer reaches. Studies encompassed both computational modelling and field experiments. Computational simulations were carried out using an existing one-dimensional, two-phase, finite-volume fate/transport model (CORAL) designed to predict gas-liquid mass transfer along uniform sewer reaches. Investigations were made into the impact of ventilation magnitude and patterns on overall mass removal, and the model's sensitivity to system hydrodynamics. Simulated sewer reaches, up to one kilometer in length, were found to be relatively insensitive to spatial variation in ventilation and system hydrodynamics, while the magnitude of ventilation was observed to have a strong impact on overall mass removal. Tracer studies were completed in two operating sanitary sewers under a wide range of experimental conditions. Back-calculated experimental mass transfer coefficients were used in conjunction with data obtained from existing literature to evaluate the semi-empirical mass transfer coefficient model which forms the basis of the computational fate/transport model. Model prediction of mass transfer coefficients proved reasonable across all scenarios. Even along an extreme sewer channel slope of 3.5%, predicted and experimental mass transfer coefficients were within a factor of 2.

ACKNOWLEDGEMENTS

This overall research effort has been funded by the Ontario Ministry of the Environment and has been guided by a knowledgeable steering committee, chaired by Mr. Rob Paine.

The field experiments, conducted as part of this research, were carried out with a great deal of cooperation from the City of Guelph Department of Waterworks, headed by Mr. John Sanvido. Special thanks go out to Graham Granger and Scott Dickieson for all of their help and patience.

Of course, this work could not have been completed without the contribution of many other individuals. I wish to thank my supervisor, Dr. Richard Corsi, for his knowledge, support, and encouragement, and the other members of my advisory committee, Drs. Gordon Hayward and Warren Stiver for their sincere interest and valuable input regarding my work.

I would also like to thank Sandra Ausma, Graham Gagnon, Perry Martos, Chris Quigley, Jennifer Shepherd, and Doug Thompson for all of their time and effort, both in the field, and in the laboratory.

Finally, to my husband, Greg Pruner, for all of his tireless help, physical and emotional support and for understanding what this has meant to me, thank you.

TABLE OF CONTENTS

List of Tables	iv
List of Figures	v
Nomenclature	vi
1. Introduction.....	1
1.1 Research Objectives	2
1.2 Scope of Research	2
1.3 Organization	3
2. Background	4
3. Theoretical Basis	9
3.1 Gas Liquid Mass Transfer	9
3.1.1 Gas-Liquid Mass Transfer Coefficients	13
3.2 Factors Affecting Gas-Liquid Mass Transfer Along Sewer Reaches	16
4. Modelling	19
4.1 Hydrodynamics	21
4.2 Ventilation.....	25
4.2.1 Magnitude of Ventilation	25
4.2.2 Ventilation Patterns	30
4.3 Multi-Parameter Analysis	36
5. Field Experiments.....	38
5.1 Overview.....	38

5.2 Site Descriptions.....	39
5.3 Experimental Methodology.....	41
5.3.1 System Hydrodynamics and Wastewater Flow Rates.....	44
5.3.2 Sewer Reach Ventilation.....	48
5.3.4 VOC Tracer Compounds.....	51
5.3.4 Experimental Conditions.....	59
5.3.5 Back-Calculation of Experimental Mass Transfer Coefficients.....	61
5.4 Experimental Results and Discussion.....	64
5.4.1 System Hydrodynamics and Wastewater Flow Rates.....	64
5.4.2 Sewer Gas Flow Rates.....	66
5.4.3 VOC Tracer Results.....	68
5.4.4 Mass Transfer Coefficients.....	76
5.4.5 Uncertainties	80
6. Conclusions.....	85
7. Recommendations.....	88
8. References.....	90
Appendix A: Calibration Curves	96
Appendix B: Experimental Results	113
Appendix C: Conference Paper	133

LIST OF TABLES

Table 4.1 - Scenarios Tested During System Hydrodynamics Analysis.....	22
Table 4.2.1 - Scenarios Tested for Magnitude of Ventilation Analysis.....	26
Table 4.2.2 - Mass Transfer Coefficients and Ventilation Rates for Ventilation Pattern Analysis	33
Table 5.2.1 - Physical Characteristics of Experimental Reaches.....	40
Table 5.3.1 - Physicochemical Properties of Experimental Tracer Compounds	52
Table 5.4.1 - Wastewater Flow Conditions	66
Table 5.4.2 - Sewer Gas Flow Rates	67
Table 5.4.3 (a) - Results of Experiment 1.1	69
Table 5.4.3 (b) - Results of Experiment 1.2	70
Table 5.4.3 (c) - Results of Experiment 1.3	71
Table 5.4.3 (d) - Results of Experiment 2.1	72
Table 5.4.4 - Supplementary Checks to Experimental VOC Analyses	73
Table 5.4.5 - Mass Balances	75
Table 5.4.6 - Operating Characteristics of Experimental Sewer Reaches.....	77
Table 5.4.7 - Experimental and Predicted Mass Transfer Coefficients.....	78
Table 5.4.8 - Individual Uncertainties	83
Table 5.4.9 - Overall Uncertainties	84

Figure 4.2.1 - Predicted Mass Removal of Chloroform Under Low and High Ventilation Rates (Plug Flow Condition)	26
Figure 4.2.2 - Predicted Mass Removal of Trichloroethylene Under Low and High Ventilation Rates (Plug Flow Condition)	27
Figure 4.2.3 - Predicted Mass Removal of Carbon Tetrachloride Under Low and High Ventilation Rates (Plug Flow Condition)	27
Figure 4.2.4 - Ventilation Patterns Simulated in this Study	32
Figure 4.2.5 - Fractional Mass Removal vs. Ventilation Pattern for Scenario 1	34
Figure 4.2.6 - Fractional Mass Removal vs. Ventilation Pattern for Scenario 2	34
Figure 4.2.7 - Fractional Mass Removal vs. Ventilation Pattern for Scenario 3	35
Figure 4.2.8 - Fractional Mass Removal vs. Ventilation Pattern for Scenario 4	35
Figure 5.2.1 - Sketch Indicating Locations of Experimental Reaches	40
Figure 5.3.1 - Guelph Experimental Reach #1	42
Figure 5.3.2 - Guelph Experimental Reach #2	43
Figure 5.3.3 - Blower Apparatus Used to Ventilate Experimental Reaches	49
Figure 5.3.4 - Purging Vessel Setup	57
Figure 5.4.1 - System Hydrodynamics for Experiment 1.3	65

A	Interfacial area available for gas-liquid mass transfer, $[L^2]$
C_g	Mass concentration in gas phase, $[M/L^3]$
C_l	Mass concentration dissolved in liquid phase, $[M/L^3]$
C_{l0}	Initial (upstream) concentration of VOC in the liquid phase, $[M/L^3]$
D_g	Gas-phase molecular diffusion coefficient, $[L^2/T]$
D_l	Liquid-phase molecular diffusion coefficient, $[L^2/T]$
D_{li}	Liquid molecular diffusion coefficient for compound i, $[L^2/T]$
D_{lO}	Liquid molecular diffusion coefficient for oxygen, $[L^2/T]$
F	Froude number, [-]
G	Ratio equal to $Q_v H_c / V_l K$
H_c	Dimensionless Henry's law constant, $[(M/L^3)_{gas} / (M/L^3)_{liquid}]$, listed as dimensionless within the body of the text
k_g	Gas-phase mass transfer coefficient, $[L/T]$
k_l	Liquid-phase mass transfer coefficient, $[L/T]$
k_{li}	Liquid-phase mass transfer coefficient for compound i, $[L/T]$
k_{lO}	Liquid-phase mass transfer coefficient for oxygen, $[L/T]$
K	Overall mass transfer coefficient, on a liquid-phase basis, $[L/T]$
K_{ow}	Octanol-water partition coefficient, [-]
K_{O_2}	Overall mass transfer coefficient for oxygen, $[m/s]$
n	Exponent which varies from 0.5 to 1.0 depending on the degree of liquid agitation, [-]
Q_v	Gas ventilation rate, $[L^3/T]$
r	Surface renewal rate, $[1/T]$
R	Rate of mass transfer across a gas-liquid interface, $[M/T]$
S	Slope of the energy gradient, $[m/m]$

U	Mean velocity of the wastewater, [m/s]
V_l	Liquid (wastewater) volume, [L ³]
x	Distance along sewer reach, [L]
δ_g	Gas film thickness, [L]
δ_l	Liquid film thickness, [L]
ψ	Ratio of liquid-phase mass transfer coefficients, [-]
γ	Temperature correction factor, [-]

In recent years, the fate of volatile organic compounds (VOCs) in wastewater has become a concern for many municipalities, industries and regulatory agencies. These concerns stem from the extensive use of VOCs, and the health risks associated with their occurrence in water and air. Prolonged exposure to low concentrations of many VOCs, e.g., benzene, tetrachloroethylene, and vinyl chloride, can lead to significantly increased cancer risk (Seinfeld, 1986). Additional concerns stem from the fact that many VOCs are classified as reactive organic gases (ROGs) which contribute to the formation of ozone in urban airsheds.

The fate of VOCs in sewers is governed by a number of complex mechanisms, including adsorption/desorption to/from solid particles, absorption in immiscible liquids, aerobic and/or anaerobic biodegradation, chemical and biological formation, and gas-liquid mass transfer. Each of these mechanisms in itself is extremely complex. Interaction amongst them compounds the problem of predicting the fate of VOCs in sewers. All of these processes play a role in either transporting or transforming VOCs, but their relative importance depends on individual sewer and wastewater characteristics, as well as the physicochemical properties of individual compounds. In addition, analysis of an entire wastewater collection system involves a vast network of sewer lines, junctions, and pump stations. For these reasons an extensive, multi-faceted research program is underway.

The Ontario Ministry of the Environment, the Metropolitan Works Department of Toronto, and the Wastewater Technology Centre are currently funding the development of an advanced computational model to predict the fate of VOCs in wastewater collection systems (WCS). In conjunction with model development, this funding also supports field, laboratory and pilot experiments that must be conducted in order to gain a better

understanding of several VOC fate mechanisms. A model simulating the fate of VOCs in WCS will provide a valuable link between discharges to sewers and loadings to wastewater treatment plants, offering improved predictions of influent loadings, subsequent sludge contamination, and effluent discharge levels. Therefore, this research is fundamental to the development of sewer use by-laws.

1.1 Research Objectives

This research effort focuses on gas-liquid mass transfer of VOCs along uniform sewer reaches. Its purpose was to gain a more comprehensive understanding of sewer system behaviour, with respect to this mechanism. In this context, specific research objectives were:

- 1) To utilize an existing VOC fate/transport model to predict the impact of key sewer system parameters on gas-liquid mass transfer and overall mass removal.
- 2) To design and conduct field experiments that would yield overall mass transfer coefficients for a wide range of sewer operating conditions.
- 3) To evaluate the VOC fate model, based on two sources of information a) data obtained from existing literature, b) data gained through the completion of the aforementioned experiments.

1.2 Scope of Research

The CORAL (Collection system Organic Release ALgorithm; Corsi *et al.*, 1992(b)) fate/transport model was used to complete objective 1 above. It is a two-phase,

one-dimensional, finite volume model designed to predict gas-liquid mass transfer along sewer reaches. It was utilized to explore the effects of specific system variables, such as hydrodynamics, ventilation, channel slope, relative depth of wastewater flow, and Henry's law constant on overall mass removal and gas-liquid mass transfer coefficients. Computational modelling facilitated rigorous sensitivity analyses and the identification of conditions that can lead to relatively high VOC emissions.

Field experiments were completed in two municipal sewer reaches. These experiments involved injecting known amounts of volatile tracers into the liquid-phase of a sewer reach and then collecting steady-state gas and liquid samples downstream of the injection point. Time and resource constraints limited field work to a total of four experiments, involving two tracer compounds, deuterated chloroform and 1,1,1-trichloroethane.

1.3 Organization

Chapter 2 provides background information on the occurrence and levels of VOCs in WCS and previous studies into gas-liquid mass transfer along sewer reaches. Chapter 3 describes the theoretical aspects of gas-liquid mass transfer which were used as the basis of this research as well as specific physical and chemical factors affecting gas-liquid mass transfer along sewer reaches. Details and results of the computational modelling which was carried out are discussed in Chapter 4. Experimental and analytical methods, experimental results and discussion of the results are included in Chapter 5. Chapters 6 and 7 address conclusions and recommendations arising from this research.

Volatile organic compounds are a class of chemicals exhibiting high Henry's law constants (e.g., $> 10^{-3}$ atm·m³/mol, or > 0.1 [-]). These high Henry's law constants are generally associated with high compound vapour pressures (e.g., > 50 mm Hg at 25 °C), low boiling points (e.g., < 150 °C at 1 atm), and low solubilities in water (e.g., $< 10,000$ mg/L).

Volatile organic compounds are used principally as industrial and commercial solvents, but they are also used in a wide variety of consumer products such as household cleaners, paints, pharmaceutical products and fuel additives. In fact, their use is so common that 8 of the 11 hazardous compounds estimated to be discharged in the greatest quantities to sewers in the United States are classified as VOCs (USEPA, 1986). These top eight compounds include dichloromethane, trichloroethane, toluene, ethylbenzene, trichloromethane, benzene, trichloroethylene, and tetrachloroethylene.

Over the past ten years, close attention has been paid to aqueous discharges and gaseous emissions of VOCs from industrial facilities and wastewater treatment plants (Bell *et al.*, 1988; Corsi *et al.*, 1987; Melcer *et al.*, 1989; Namkung and Rittmann, 1987; Pincince, 1989). Recent studies by Chang *et al.* (1987) and Corsi (1989) have also recognized the potential for VOC emissions from WCS. These complex physical, chemical and biological networks receive a host of VOCs and encompass vast numbers of openings to the ambient atmosphere.

Evidence of the occurrence and levels of VOCs in municipal sewers has been provided by monitoring events carried out at numerous locations. Levins *et al.* (1979)

monitored aqueous concentrations of priority pollutants in the wastewater collection systems of Atlanta, Cincinnati, Hartford and St. Louis. A total of 5 industrial, 10 commercial, and 11 residential sewers were monitored, in addition to tap water and treatment plant influent. Over all, thirteen VOCs were detected. Average concentrations for individual VOCs within residential and commercial sewers were 10 $\mu\text{g/L}$ and 25 $\mu\text{g/L}$, respectively. Concentrations in sewers accepting industrial discharges ranged from less than 1 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$, with average aqueous concentrations of ethylbenzene, tetrachloroethylene, toluene, 1,1,1-trichloroethane, and trichloroethylene exceeding 50 $\mu\text{g/L}$.

Volatile organic compounds are also found in the gaseous phase of municipal sewers. Huang *et al.* (1979) collected sewer off-gas from a main interceptor to the Sacramento (California) Main Treatment Plant in order to evaluate the effectiveness of activated carbon adsorption for sewer odour control. All samples were analyzed by GC/FID to determine total hydrocarbon concentrations. The results of four sampling events indicated the presence of 59, 531, 76, and 13 ppm total hydrocarbon. Across the samples, compounds with 8 or more carbon atoms prevailed.

Reid and McEvoy (1987) examined sewer atmospheres in London, England. In a sewer receiving relatively small amounts of industrial effluent, gaseous benzene, trichloroethylene, and toluene levels were <0.5, <0.5 and 5 parts per million by volume (ppmV), respectively. However, in a sewer reported to contain a high level of industrial wastewater, gaseous concentrations of these same three compounds reached 52, 116, and 170 ppmV, respectively.

Whitmore *et al.* (1992) completed monitoring in a heavily industrialized municipal sewer in Toronto, Ontario. Although it was apparent that the sewer reach experienced

significant ventilation (e.g. several well-perforated manholes had physically detectable outflows), gaseous concentrations of many VOCs during initial monitoring events were extremely high. Concentrations of 7 aromatic VOCs exceeded 15 ppmV. Concentrations of toluene, 3-ethyltoluene, and 1,2,4-trimethylbenzene were 44, 39, and 35 ppmV, respectively. Subsequent monitoring along this same sewer reach has led to emissions estimates of over 1000 kg/yr for individual VOCs such as toluene (Corsi *et al.*, 1992(c)).

Gas-liquid mass transfer in sewers depends to varying extents on physical phenomena that occur in bulk liquid, near the gas-liquid interface and in the bulk gas comprising a sewer headspace. For the latter, gas exchange between the sewer and ambient atmosphere can have a significant effect on overall mass transfer.

Ventilation of wastewater collection systems is a mechanism that remains, for the most part undocumented. Determining the magnitude of forced ventilation, undertaken to eliminate odours or to facilitate personnel entry, is relatively straight forward. Determining the magnitude and pattern of natural ventilation, on the other hand, is extremely difficult. Some work was completed by Pescod and Price (1981) to identify physical factors which contribute to the natural ventilation of sewers. Factors included wastewater drag at the gas-liquid interface, eduction by wind, buoyancy effects due to temperature differences between the sewer and ambient atmospheres, rise and fall of wastewater due to temporal variations in flow and barometric pressure gradients. Corsi (1989) studied these factors and their combined effects along hypothetical sewer flow circuits. He reported that for combined sanitary/storm sewers, high gas flow rates can be expected to prevail. In addition, for small diameter systems with many vents, such as those observed in residential areas, gas velocities should be relatively high, while for moderate to large diameter sewers, particularly sanitary interceptors, gas velocities should remain low in relation to wastewater velocity.

As with ventilation, few researchers have investigated gas-liquid mass transfer along uniform sewer reaches. However, oxygen's importance as a life-supporting element of natural water bodies has led, over several decades, to extensive investigation of oxygen mass transfer along rivers and streams (Cadwaller and McDonnell, 1969; Krenkel and Orlob, 1962; Streeter, Wright and Kehr, 1936; Tsivoglou and Neal, 1976). Parkhurst and Pomeroy (1972) completed oxygen transfer experiments along 12 operating sewers in Los Angeles, California. Their research led to the only published model to predict reaeration coefficients within sewer environments. Although the model predicts oxygen mass transfer based on a number of physical parameters, it does not account for biological oxygen demand. The authors chose to circumvent the problem of biological activity by shock loading the experimental sewer reaches with caustic soda 24 hours prior to testing, and feeding hypochlorite into the wastewater during each test. A description of their model is provided in the next chapter.

Jensen and Hvitved-Jacobsen (1990) developed a method for measuring oxygen mass transfer coefficients in gravity sewers using radiotracers. Theirs was a direct method involving the use of a gaseous tracer, krypton-85, and a non-gaseous tracer, tritium (T_2O), which served as an indicator of dispersion. Krypton-85 was assumed to have a mass transfer coefficient that was constant relative to that of oxygen, under the conditions tested. A krypton mass transfer coefficient to oxygen mass transfer coefficient ratio had been determined in a previous study by Tsivoglou *et al.* (1965). Aqueous concentration ratios of krypton-85 to tritium at upstream and downstream stations were used to determine the krypton-85 mass transfer coefficients along a 2.3 km sewer reach (0.6-0.7 m diameter) in Aalborg, Denmark. Application of Parkhurst and Pomeroy's model to their experimental conditions resulted in a predicted reaeration coefficient that was within 21% of the experimentally determined reaeration coefficients over three experiments.

Corsi (1989) is the only researcher to date to have specifically targeted gas-liquid mass transfer of VOCs along sewer reaches. He completed six mass transfer experiments in two different reaches in California, utilizing deuterated chloroform as a volatile tracer. He predicted chloroform mass transfer coefficients by combining Parkhurst and Pomeroy's model with an adjustment factor which accounts for differences in liquid molecular diffusivities of two given compounds. Coefficients predicted in this manner were within +/- 33% of experimentally determined mass transfer coefficients.

Numerous theories have been developed to describe gas-liquid mass transfer and associated mass transfer coefficients. These models vary in their treatment of gas and liquid phases, physical parameters and boundary conditions. The most common of these theories are presented below.

3.1 GAS LIQUID MASS TRANSFER

Mass transfer across a gas-liquid interface is often explained using two-film theory (Lewis and Whitman, 1924). This theory assumes that mass transfer takes place via steady-state molecular diffusion through two thin films, one gas and one liquid, separated by a gas-liquid interface. Performing a mass balance on the system, assuming that the bulk gas and liquid phases are well-mixed and that no mass is allowed to accumulate at the gas-liquid interface, leads to the development of Equation 1.

$$R = K A \left(C_1 - \frac{C_g}{H_c} \right) \quad (1)$$

Where R = Rate of mass transfer across interface, $[M/T]$

K = Overall mass transfer coefficient, on a liquid-phase basis, $[L/T]$

A = Interfacial area, $[L^2]$

C_1 = Mass concentration dissolved in liquid phase, $[M/L^3]$

C_g = Mass concentration in gas phase, $[M/L^3]$

H_c = Dimensionless Henry's Law constant, $[(M/L^3)_{\text{gas}}/(M/L^3)_{\text{liquid}}]$

The Henry's law constant in Equation 1 represents an equilibrium partition coefficient between air and water. Although the Henry's law constant, for a given compound, may be expressed as a partial pressure divided by a liquid concentration (e.g., atm·m³/mol), it is also possible to express it as the mass concentration of compound in the gas phase divided by the mass concentration of compound in the liquid phase (e.g., μg/m³/μg/m³). This non-dimensionalized form of Henry's law constant is typically referred to as the dimensionless Henry's law constant, H_C . It is generally accepted that a VOC is a compound possessing an H_C greater than 0.1.

The overall mass transfer coefficient used in this governing equation may be subdivided into its contributing components (Equation 2). Terms I and II are commonly referred to as liquid and gas-phase resistances.

$$\frac{1}{K} = \frac{1}{k_l} + \frac{1}{k_g H_C} \quad (2)$$

I II

Where k_l = Liquid-phase mass transfer coefficient, [L/T]

k_g = Gas-phase mass transfer coefficient, [L/T]

In assuming steady-state diffusion, two-film theory proposes that gas and liquid phase mass transfer coefficients are directly proportional to molecular diffusivities, i.e.,

$$k_g = \frac{D_g}{\delta_g} \quad (3a)$$

$$k_l = \frac{D_l}{\delta_l} \quad (3b)$$

Where D_g = Gas-phase molecular diffusion coefficient, $[L^2/T]$

D_l = Liquid-phase molecular diffusion coefficient, $[L^2/T]$

δ_g = Gas film thickness, $[L]$

δ_l = Liquid film thickness, $[L]$

Gas and liquid film thicknesses, δ_g and δ_l , are assumed to be inversely proportional to the degree of turbulent mixing (i.e., turbulent kinetic energy) in the bulk gas and liquid, respectively. Systems with large mixing intensities are expected to exhibit smaller film thicknesses, while quiescent systems are expected to exhibit large film thicknesses.

Other theories do not require an assumption of steady-state diffusion. Penetration (Higbie, 1935) and surface renewal (Danckwerts, 1951) theories assume non-steady-state diffusion of mass to or from a parcel of fluid over a brief interval of time in which it is located at the gas-liquid interface. Penetration theory is based on the assumption that every parcel spends an equal amount of time at the interface, while surface renewal theory predicts the residence time of a parcel according to a probabilistic "surface aging" model. Both models assume that molecular diffusion takes place into a column of fluid of infinite depth. The resulting equations for the rate of mass transfer can be expressed in identical form to Equation 1. The key difference is that for penetration and surface renewal theories the mass transfer coefficient is proportional to the square root of molecular diffusivity, as indicated in Equations 4 and 5.

$$k_l = 1.13 (D_l r)^{1/2} \quad (4) \quad \text{Penetration Theory}$$

$$k_l = (D_l r)^{1/2} \quad (5) \quad \text{Surface Renewal Theory}$$

Where r = surface renewal rate $[1/T]$, a measure of the frequency at which contaminants contact a gas-liquid interface. The value of r is assumed to be proportional to the amount of turbulent mixing in a liquid stream.

Film-penetration theory was developed by Dobbins (1964), and stems from the preceding theories. Dobbins noted that the relationship

$$k_l \propto D_l^n \quad (6)$$

can be used to describe the dependency of the liquid phase mass transfer coefficient on liquid molecular diffusivity. The exponent n is constant for each of the aforementioned theories but differs in magnitude from one to the other. It takes on a value of 1.0 for two-film theory, and a value of 0.5 for penetration and surface renewal theories. However, Dobbins argued that experimental data indicate that n is actually a variable. For this reason, he proposed a new mathematical model that relies on the "surface aging" concept proposed by Dankwerts' surface renewal theory, but assumes that molecular diffusion takes place across a liquid film of finite thickness, L . Again, the resulting equation for the rate of mass transfer is identical in form to Equation 1. However, the mass transfer coefficient is described by a hyperbolic function, as indicated in Equation 7.

$$k_l = (D_l r)^{1/2} \coth (r L^2/D_l)^{1/2} \quad (7)$$

Examination of Equation 7 indicates that two-film and penetration models of k_l are special limiting cases of film-penetration theory. As the value of the surface renewal rate

approaches zero, n tends to 1.0 (two-film theory). As the values of surface renewal rate and film thickness increase, n tends to 0.5 (penetration and surface renewal theories).

As with Equations 3a and 3b, expressions similar to Equations 4 through 7 can be used to estimate k_g , if D_g is substituted for D_l and r is assumed to be the surface renewal rate for air parcels. However, the second term on the right hand side of Equation 2 becomes small relative to $\frac{1}{k_l}$ when the product $k_g H_C \gg k_l$. For some systems, particularly diffused bubble aeration and mechanical surface aeration of wastewater, $\frac{k_g}{k_l}$ values have been noted to be much lower than 100 (Munz and Roberts, 1989). Under these conditions, liquid-phase domination of mass transfer is only achieved for high values of H_C ($H_C \gg 0.1$). However, for many other systems, $\frac{k_g}{k_l}$ has been reported to be greater than 100. In such cases, liquid-phase resistance represents more than 90% of the overall resistance to mass transfer; when $H_C > 0.1$. It is assumed in this study that liquid-phase resistance to mass transfer dominates the overall mass transfer process, i.e., the overall mass transfer coefficient, K , is approximately equal to the liquid-phase mass transfer coefficient, k_l .

3.1.1 Gas-Liquid Mass Transfer Coefficients

Of all of the variables presented in Equation 1, the mass transfer coefficients, K , k_l and k_g remain the most difficult to routinely quantify. With VOCs, concern rests primarily in obtaining a value for k_l . Although key factors affecting the liquid phase mass transfer coefficient, such as surface renewal rate, and degree of turbulent mixing have been

identified, the means to determine their effect on a real, dynamic system does not exist. For this reason, numerous empirical and semi-empirical models have been developed to predict mass transfer coefficients for open channels. The majority have dealt with the transfer of oxygen in clean water systems. A conceptual model for reaeration of natural streams was developed by O'Connor and Dobbins (1958). This was followed by other models by Cadwaller and McDonnell (1969) and Tsivoglou and Neal (1976). As indicated previously, Parkhurst and Pomeroy (1972) developed the only model for mass transfer within sewer environments. Theirs is a semi-empirical model, based on field experiments conducted in 12 operating sewers. According to their model

$$K_{O_2} = 2.67 \times 10^{-4} (1 + 0.17F^2) \gamma (SU)^{3/8} \quad (8)$$

Where F = Froude number, [-]

γ = temperature correction factor, [-]

K_{O_2} = overall mass transfer coefficient for oxygen, [m/s]

S = slope of the energy gradient, [m/m]

U = mean velocity of the wastewater, [m/s]

For gases with very low solubility in water and large Henry's law constants, such as oxygen, the gas film offers relatively little resistance to mass transfer. Therefore, the overall oxygen mass transfer coefficient, K_{O_2} , provided by this model is approximately equal to the liquid-phase mass transfer coefficient for oxygen, k_{lO} .

Parkhurst and Pomeroy's model accounts for many of the factors known to influence a mass transfer coefficient. The Froude number is a dimensionless group representing the ratio of inertial forces to gravitational forces. It provides an indication of

the amount of energy at a free surface. Therefore, the term $0.17F^2$ in Equation 8 allows for the adjustment of a mass transfer coefficient due to changes in the degree of surface disturbance and corresponding changes in surface area at a gas-liquid interface. The temperature correction factor, γ , provides for increased mass transfer caused by warmer wastewaters. Incorporation of channel slope and mean wastewater velocity account for the degree of turbulent mixing in a system. The product US represents the rate of dissipation of potential energy as wastewater travels down a sewer reach. It is reasonable to assume that a large fraction of the dissipated potential energy is converted to turbulent kinetic energy, which enhances turbulent mixing and gas-liquid mass transfer.

Predictions of oxygen mass transfer coefficients allow subsequent estimation of liquid-phase mass transfer coefficients for other compounds using the relationship

$$\psi = \frac{k_{li}}{k_{lo}} = \left\{ \frac{D_{li}}{D_{lo}} \right\}^n \quad (9)$$

Where ψ = Ratio of liquid-phase mass transfer coefficients, [-]

D_{li} = Liquid molecular diffusion coefficient for compound i, [L^2/T]

D_{lo} = Liquid molecular diffusion coefficient for oxygen, [L^2/T]

k_{li} = Liquid-phase mass transfer coefficient for compound i, [L/T]

k_{lo} = Liquid-phase mass transfer coefficient for oxygen, [L/T]

n = Exponent which varies from 0.5 to 1.0 depending on the degree of liquid agitation, [-]

This relationship proves valuable for estimation of VOC mass transfer coefficients, because values of ψ , or D_l and D_{lo} , and k_{lo} for many VOCs and oxygen are available.

Even when a specific value of ψ is unknown it has been shown that for compounds with $H_c > 0.1$, ψ generally ranges from 0.5 to 0.7 in natural surface waters and wastewater (Matter-Muller *et al.*, 1981; Smith *et al.*, 1980). Again, Equation 9 relates only to liquid-phase mass transfer coefficients which can be equated to overall mass transfer coefficients if gas-phase resistance is negligible.

3.2 FACTORS AFFECTING GAS-LIQUID MASS TRANSFER ALONG SEWER REACHES

Equation 1 may be used to describe gas-liquid mass transfer of VOCs between wastewater and sewer atmospheres along a uniform sewer reach. However, there are numerous factors that must be assessed prior to employing it.

Sewer line characteristics affect mass transfer of VOCs for a number of reasons. Inspection of Equation 1 indicates that several variables are influenced by changes in sewer geometry and wastewater flow conditions. For example, relative depth of wastewater flow, which is defined here as the perpendicular distance from channel invert to wastewater surface, divided by pipe diameter, affects the surface area available for mass transfer and the total volume of headspace above the wastewater surface. Larger headspace volumes associated with lower relative depths, effectively dilute gaseous concentrations of VOCs, lowering C_g and increasing the concentration driving force, $(C_l - \frac{C_g}{H_c})$. Alternately, small gas volumes associated with high relative depths result in elevated gaseous concentrations, which lower the concentration driving force. In addition, relative depth influences the liquid phase mass transfer coefficient because it alters the

surface renewal rate and degree of turbulent mixing within wastewater. Pipe diameter also affects surface area and overall gas volume.

Sewer channel slope and relative roughness affect uniform flow characteristics, and thus influence overall mass transfer for several reasons. First, reaches with steep slopes are expected to exhibit higher mass transfer coefficients due to higher wastewater mean velocities and increased turbulent mixing. Second, because slope also affects the relative depth of wastewater flow, it will indirectly affect the mixing length, i.e., the length through which liquid parcels must travel to reach a gas-liquid interface. Shorter mixing lengths facilitate gas-liquid mass transfer. Third, as mentioned in the previous paragraph, changes in relative depth are associated with changes in gas volume. Therefore, changes in sewer channel slope also indirectly influence gaseous concentrations of VOCs. Finally, because sewer channel slope affects wastewater mean velocity, it also indirectly affects the degree of natural ventilation experienced along a reach. This is a result of a liquid drag phenomenon as reported by Pescod and Price (1981). According to their research, the higher mean wastewater velocities associated with steep channel slopes can be expected to induce greater horizontal transport of air, enhancing natural ventilation of sewers.

The physicochemical properties of VOCs within wastewater are a primary factor affecting gas-liquid mass transfer. For VOCs with high Henry's law constants, the second term in brackets in Equation 1, C_g/H_c , is reduced. This augments the concentration driving force, effectively increasing the rate of mass transfer. Higher values of H_c are also associated with lower gas-phase resistance and, hence, higher overall mass transfer coefficients.

Variables within Equation 1 are also influenced by physical and chemical characteristics of wastewater. Warmer wastewater temperatures increase the liquid phase

mass transfer coefficient, k_L , and Henry's law constant, H_C (Gossett, 1987; Ashworth, 1988). Surfactants alter surface tension at a gas-liquid interface. Depending on the situation, they can either reduce or increase the interfacial area available for mass transfer, potentially accelerating or retarding the rate of mass transfer. Surfactants may also add an additional barrier to mass transfer at the gas-liquid interface. Finally, the presence of solids or attached or suspended microorganisms can reduce gas-liquid mass transfer by direct competition for VOC mass, and subsequent reductions in C_L .

Ventilation affects overall mass transfer between liquid and gas because of its impact on gas-phase concentration, C_g . In well-ventilated systems, gas concentrations typically remain small, diluted by incoming fresh air. In poorly ventilated systems gas concentrations can become elevated, as mass is allowed to accumulate in the head space. The diversity and complexity of wastewater collection systems have been a major obstacle to successfully quantifying factors that affect their ventilation. Most systems are naturally ventilated, although some have been artificially ventilated, generally to prevent H_2S formation. For those naturally ventilated systems, the number of openings which allow gas exchange between sewer and ambient atmospheres affects the degree of ventilation. Ventilation rates are expected to be highest in combined sanitary/storm systems and in residential areas with many house vents and short distances between manhole covers. Corsi (1989) reported that for these types of reaches, liquid drag and eduction by wind are likely to be dominant ventilation mechanisms. For a 0.25 m ID pipe, he estimated that liquid drag and eduction by wind induce gas mean velocities ranging from 0.04 - 0.20 m/s, and 0.029 - 1.2 m/s, respectively. Ventilation rates are expected to be lowest for large sanitary interceptors. For this category of sewer, rise and fall of wastewater can be a relatively important ventilation mechanism. Corsi (1989) estimated that, for a 1.5 m ID pipe, rise and fall of wastewater induces gas mean velocities of approximately 0.002 m/s.

No accurate mathematical models of gas-liquid mass transfer of VOCs in WCS currently exist. This is due to a lack of experimental data, and to the vast number of physical scenarios and boundary conditions that may prevail. However, a few basic analytical models have been developed to describe gas-liquid mass transfer along uniform sewer reaches. Corsi (1991), derived one analytical solution, given several simplifying assumptions:

1. Uniform ventilation of the gas-phase, i.e., equal quantities of air inflow and exhaust along the entire sewer reach.
2. No net axial movement of gas.
3. Concentration of VOC in the sewer atmosphere is much higher than the ambient concentration.
4. Convection is much greater than dispersion in the liquid-phase, i.e., ideal plug flow conditions.
5. Steady and continuous VOC discharge, wastewater flow, and gas ventilation rates.
6. Steady-state solution of VOC concentration ($t \rightarrow \infty$).

The resulting equation describing gas-liquid mass transfer under finite ventilation is:

$$C_l = C_{l0} \exp \left\{ \frac{-K}{U} \left[1 - \frac{1}{\frac{Q \cdot H_c}{V_l K} + 1} \right] x \right\} \quad (10)$$

Where C_l = Concentration of VOC in the liquid phase, $[M/L^3]$

C_{l0} = Initial (upstream) concentration of VOC in the liquid phase, $[M/L^3]$

x = Distance along sewer reach, [L]

Q_v = Gas ventilation rate, [L^3/T]

V_l = Liquid (wastewater) volume, [L^3]

Corsi re-expressed Equation 10 as:

$$C_l = C_b \exp \left\{ \frac{-K}{U} \left[1 - \frac{1}{G+1} \right] x \right\} \quad (11)$$

where

$$G = \frac{Q_v H_c}{V_l K}$$

He also showed that gas-liquid mass transfer under infinite ventilation may be described by the equation:

$$C_l = C_b \exp \left\{ \frac{-K}{U} x \right\} \quad (12)$$

These analytical solutions are valuable when assumptions listed above agree with actual system conditions. However, many of the scenarios tested as part of this research involved non-uniform ventilation and unsteady-state systems. Therefore, individual sewer reach simulations were carried out using a computational model, CORAL (Collection system Organic Release ALgorithm). This was a one dimensional, two-phase model designed to predict gas-liquid mass transfer along sewer reaches (Corsi *et al.*, 1992(b)). Mass transfer coefficients were estimated using Equations 8 and 9. Henry's law constants were estimated using wastewater temperature in conjunction with relationships derived by Gossett (1987). The computational solution treated both gaseous and liquid phases of a sewer reach as series of n continuous flow, stirred tank reactors (CFSTRs). It accommodated variable liquid and gas flow rates (and interfacial areas), variable exhaust

and intake patterns, and continuous, slug or intermittent discharges. Biodegradation and sorption effects were assumed to be negligible.

Corsi *et al.* (1992(b)) evaluated the CORAL model using data from 4 field experiments. In two of the cases, CORAL overpredicted experimental mass transfer coefficients by 18% and 28%. In the remaining cases, CORAL underpredicted experimental mass transfer coefficients by 17% and 25%. Differences of these magnitudes were considered adequate given uncertainties in sewer, wastewater and ventilation characteristics.

For this study, the CORAL model was used to complete sensitivity analyses of several system parameters on gas-liquid mass transfer. These parameters were grouped into the general categories of wastewater hydrodynamics, headspace ventilation (aerodynamics), and interfacial mass transfer coefficients. The sensitivity associated with each group is described individually below.

4.1 HYDRODYNAMICS

The sensitivity of overall mass removal to system hydrodynamics was analyzed. Hydrodynamic conditions were characterized through reactor analysis: different numbers of CFSTRs in series were used to simulate varying degrees of longitudinal dispersion. In this investigation, reach lengths of 100 m, 500 m, and 1 km were modelled. The CORAL model allotted the same number of CFSTRs to both the liquid and gas phases. Reaches were analyzed as 1, 3, 5, 10, 20, 50, and 100 CFSTRs in series, thus equaling or approaching the theoretical extremes of an instantaneously, well-mixed system (1 CFSTR) and an ideal plug-flow system (an infinite number of CFSTRs). Each hydrodynamic simulation was tested under sixteen scenarios that represented different combinations of

ventilation, channel slope, relative wastewater depth, pipe diameter and Henry's law constant. Table 4.1 provides a summary of the scenarios examined for each hydrodynamic condition. Ventilation rates are expressed in turnovers of air per day (TuPD). By convention, these turnovers were based on empty pipe volume. The wastewater temperature was fixed at 20 °C, and the relative roughness coefficient was held constant at 0.014.

Table 4.1 - Scenarios Tested During System Hydrodynamics Analysis

Scenario	Henry's Law Constant [-]	Sewer Pipe Diameter [m]	Relative Wastewater Depth [-]	Channel Slope [m/m]	Ventilation Rate [TuPD]
1	0.30	0.5	0.2	0.005	1.0
2	0.30	0.5	0.2	0.005	10.0
3	0.30	0.5	0.2	0.02	1.0
4	0.30	0.5	0.2	0.02	10.0
5	0.30	2.0	0.2	0.005	1.0
6	0.30	2.0	0.2	0.005	10.0
7	0.30	2.0	0.2	0.02	1.0
8	0.30	2.0	0.2	0.02	10.0
9	0.30	0.5	0.5	0.005	1.0
10	0.30	0.5	0.5	0.005	10.0
11	0.30	0.5	0.5	0.02	1.0
12	0.30	0.5	0.5	0.02	10.0
13	0.30	2.0	0.5	0.005	1.0
14	0.30	2.0	0.5	0.005	10.0
15	0.30	2.0	0.5	0.02	1.0
16	0.30	2.0	0.5	0.02	10.0

For the conditions simulated, the overall mass removals predicted by CORAL were found to be insensitive to hydrodynamic dispersion. For all three reach lengths, mass removals which resulted from treating the systems as single well-mixed cells or reactors were closely matched by those which resulted from treating the systems as plug-flow reactors. In fact, along a 1 km reach, the average difference in fractional mass removal which resulted from treating the system as a single well-mixed reactor, when it was actually a plug-flow system was 0.013, (1.3%).

In spite of the proximity of the results, it was possible to discern that overall mass removal along the longer reach lengths was more sensitive to these two hydrodynamic extremes. The largest variance which occurred along the 1 km reach represented a 7.4% difference in overall mass removal, while the worse case scenario along the 100 m reach represented a difference of only 0.6%.

The 7.4% difference in overall mass removal along the 1 km reach was the maximum error observed over all hydrodynamic tests. It was associated with Scenario 2. The second, third and fourth highest percentage errors were recorded for Scenarios 4, 6, and 8 along the 1 km reach and represented 5.1%, 1.8% and 1.8%, respectively. The common denominators amongst these scenarios were low relative depth of flow, and high ventilation rates.

In examining Equation 1, it can be seen that the mass transfer coefficient, K , and the interfacial area, A , are the same for both well-mixed and plug-flow conditions. However, the liquid concentration, C_l , will differ under different hydrodynamic conditions. This is because the liquid concentration within a single well-mixed reactor is assumed to be equal to the liquid concentration exiting the reactor. This results in a liquid

concentration that is lower than the average liquid concentration observed in an equivalent plug-flow reactor.

When gaseous VOC concentrations, C_g , are high, the concentration driving force $(C_l - \frac{C_g}{H_c})$ remains low and differences in liquid concentration have little impact on overall mass removal. However, larger headspace volume associated with low relative depths effectively dilute gaseous concentrations and high ventilation rates produce even greater dilution of gas phase VOCs. Under these conditions, as in Scenarios 2, 4, 6, and 8, where gaseous VOC concentrations are small, the concentration driving force is dominated by C_l , and differences in liquid concentration have an observable impact on overall mass removal. Therefore, although system hydrodynamics were predicted to have little effect on overall mass removal from uniform sewer reaches less than 1 km in length, caution should be exercised in extending this finding to longer reaches with exceptionally low relative depths (<0.2) and high ventilation rates (>10 TuPD).

This demonstrated insensitivity means that relatively long sewer reaches may be treated as single reactors, without incurring large errors in estimated VOC emissions. This is particularly true considering the high uncertainties in other parameters (e.g., magnitude of ventilation), required for emissions estimates. Since computational models typically step through a sewer reach reactor by reactor, modelling run time is reduced when a reach is treated as one well-mixed reactor, rather than many reactors (PFR). Although the time savings are minimal when a single reach is modelled, reductions in computational run time could be substantial when modelling overall mass removal from an entire wastewater collection system.

4.2 VENTILATION

The sensitivity of overall mass removal to changes in headspace ventilation was modelled. This segment of modelling was divided into two parts. The first examined sensitivity to the magnitude of ventilation along a sewer reach. The second examined sensitivity to spatial ventilation patterns. Analysis was restricted to cocurrent flow, where gas and liquid streams travel in the same direction. This was a limitation of CORAL.

4.2.1 Magnitude of Ventilation

To examine the effects of ventilation magnitude on mass transfer, a 1 km reach length was used. Both well-mixed and near plug flow systems were simulated (1 CFSTR, and 100 CFSTRs). Magnitudes of one volume turnover per day and ten volume turnovers per day were tested (TuPD). Three different volatile compounds were examined, chloroform, trichloroethylene, and carbon tetrachloride. At 20 °C these compounds exhibit dimensionless Henry's law constants of 0.12, 0.30 and 0.97, respectively (Gossett, 1987). Two minute slug discharges of 100 µg/L (resulting concentration in wastewater) were simulated. A summary of the scenarios tested is provided in Table 4.2.1. Additional model runs were completed to assess the maximum overall mass removal that would be observed if the reach was entirely open to the atmosphere (infinite dilution). Although the assumption of infinite dilution is not believed to be realistic for most sewer reaches, it does provide a reference value for assessing the mass removal achieved under different degrees of finite ventilation. Modelling results are presented in Figures 4.2.1 through 4.2.3. Overall mass removals are expressed as a percentage of the overall mass removal achieved during infinite dilution conditions. Results for well-mixed and plug-flow conditions differed by less than 5%. Therefore only the results for a plug-flow system have been included in this section.

Table 4.2.1 - Scenarios Tested for Magnitude of Ventilation Analysis

Scenario	Sewer Pipe Diameter [m]	Relative Wastewater Depth [-]	Channel Slope [m/m]
1	0.5	0.2	0.005
2	0.5	0.2	0.02
3	2.0	0.2	0.005
4	2.0	0.2	0.02
5	0.5	0.5	0.005
6	0.5	0.5	0.02
7	2.0	0.5	0.005
8	2.0	0.5	0.02

Wastewater temperature = 20 °C, relative roughness coefficient = 0.014.

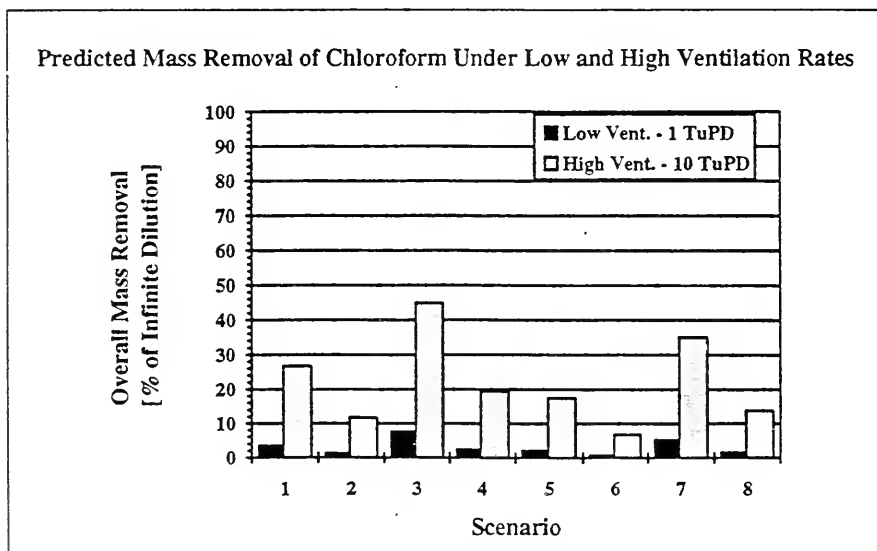


Figure 4.2.1 - Predicted Mass Removal of Chloroform Under Low and High Ventilation Rates (Plug Flow Condition)

Predicted Mass Removal of Trichloroethylene Under Low and High Ventilation Rates

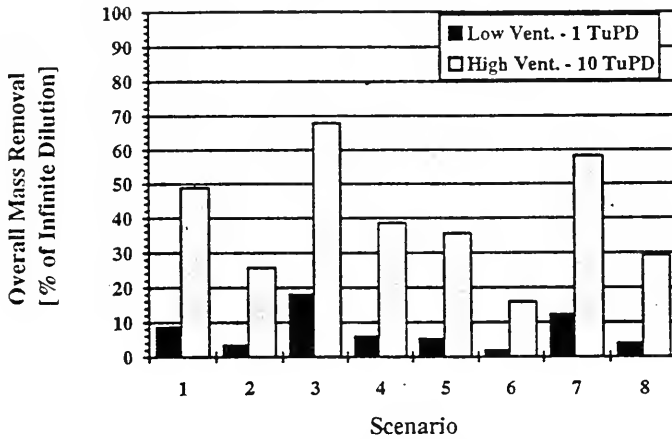


Figure 4.2.2 - Predicted Mass Removal of Trichloroethylene Under Low and High Ventilation Rates (Plug Flow Condition)

Predicted Mass Removal of Carbon Tetrachloride Under Low and High Ventilation Rates

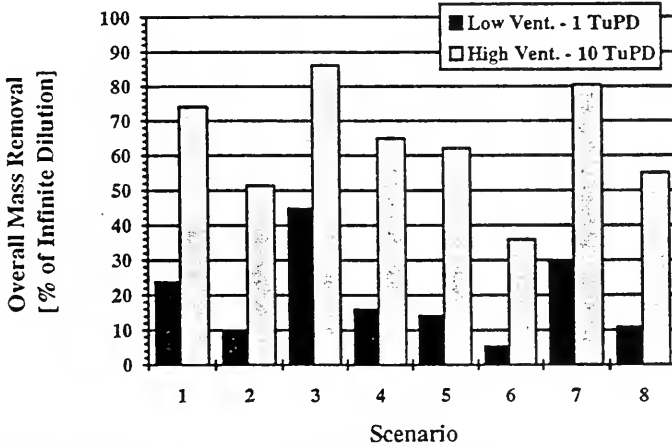


Figure 4.2.3 - Predicted Mass Removal of Carbon Tetrachloride Under Low and High Ventilation Rates (Plug Flow Condition)

Overall mass removal is highly sensitive to the magnitude of ventilation experienced by the system. An order of magnitude increase in ventilation led to an average 700%, 540%, and 320% increase in overall mass removal for chloroform, trichloroethylene and carbon tetrachloride, respectively, for the 8 conditions which were simulated. Carbon tetrachloride exhibited the largest absolute increases, including an increase representing 51% of the mass removal under infinite dilution (Scenario 7). Figures 4.2.1 through 4.2.3 suggest the importance of correctly determining the magnitude of ventilation experienced by a sewer reach, if one is to accurately estimate VOC emissions from WCS.

Significant increases in mass removal due to increased ventilation can occur. However, there is almost a two-fold difference between the average percentage increases of chloroform and carbon tetrachloride. This indicates the importance of compound physicochemical properties in emissions from sewers. For chloroform, a relatively low volatility VOC, saturation of a sewer reach headspace is achieved more rapidly than for high volatility VOCs such as carbon tetrachloride. Without adequate ventilation, saturation of the headspace becomes the limiting factor in overall mass removal. When the ventilation rate is increased by a factor of 10, the saturation limitation is lowered and the mass transfer coefficient becomes a limiting factor. For carbon tetrachloride, saturation of the sewer headspace plays a far less limiting role in overall mass removal and the mass transfer coefficient is a significant factor. Therefore, when the ventilation rate is significantly increased, no substantial change in the limiting factors is observed and a smaller percentage increase in overall mass removal results.

This relationship between overall mass removal, ventilation rate and volatility can also be explained using the simple analytical solution presented in Equation 11. When wastewater flow rate (V_f , U) and mass transfer coefficient, K, are fixed, mass removal

becomes a function of Q_V and H_C . In fact, for large Q_V or H_C , G becomes large and the infinite ventilation condition (Equation 12) is approached. For a high volatility compound such as carbon tetrachloride, the product $Q_V H_C$ will be large for most sewer ventilation rates, and the infinite ventilation (dilution) condition is approached. Subsequent order of magnitude increases in ventilation rate will increase overall mass removal, but as the infinite ventilation case is asymptotically approached, only moderate or small percentage increases will be observed. However, for a lower volatility VOC, such as chloroform, the product $Q_V H_C$ will be small and order of magnitude increases in ventilation rate should produce large increases in overall mass removal, up to the point where the infinite ventilation condition is approached.

Expression of overall mass removal as a percentage of mass removal achieved during infinite dilution conditions provides a baseline for comparison. It does not, however, provide information regarding the fraction of discharged mass which is ultimately removed along a sewer reach. For this series of model simulations, the highest fractional removals were observed for Scenario 1, under high ventilation conditions. Fractional mass removals (mass removed from reach/total mass discharged to reach) of 0.088, 0.16, and 0.26 were predicted for chloroform, trichloroethylene and carbon tetrachloride, respectively. However, these fractional mass removals were not typical of those observed under the remaining scenarios. For the majority of scenarios tested, fractional mass removal was under 0.07. The lowest fractional removals were observed for Scenario 8. Under low ventilation conditions, fractional removals of 0.00041, 0.0010, and 0.0032 were predicted for chloroform, trichloroethylene and carbon tetrachloride, respectively. Therefore, although increased rates of ventilation led to significant percentage increases in overall mass removal, the relative magnitude of mass removal under the majority of scenarios was low ($< 7\%$) along the hypothetical 1 km sewer reach which was used.

4.2.2 Ventilation Patterns

Corsi (1989) investigated the effects of spatial distribution of ventilation on VOC emissions from sewers. He studied five different ventilation patterns, noting both overall mass removal and emissions from specific exhaust locations. Results suggested that although spatial patterns and specific outflow locations might be important in terms of localized health concerns, spatial distribution of ventilation had little effect on total VOC emissions from a relatively long hypothetical sewer reach.

Corsi's examination was, however, limited in scope. Simulations were carried out on a single hypothetical sewer reach, 5 km in length, and 1.0 m in diameter. Sewer channel slope was 0.2%, relative depth of flow was 0.25 and ventilation rate was held at 5.0 TuPD. A single compound with a dimensionless Henry's law constant of 0.75 was studied. For this study, additional computational analyses were completed to investigate a far broader range of parameters.

As in Corsi's research, cell-specific inflows and outflows were used to describe air circulation, and to determine the effects of ventilation patterns on VOC emissions from sewers. In the interest of achieving discernable mass removals, a 2 km reach length was used. Plug flow conditions were assumed. However, in order to reduce extensive model run time, only 50 CFSTRs were placed in series. As in the previous section, chloroform, trichloroethylene, and carbon tetrachloride were examined and two minute slug discharges of 100 $\mu\text{g/L}$ (resulting concentration in wastewater) were simulated. Three ventilation patterns were tested. These patterns were: 1) flow-through, where atmospheric air enters the first cell (upstream end of reach) and exits through the last cell in series (downstream end of reach), 2) multiple-cell inflow/outflow, where several air flow circuits are established along the reach as air enters and exits at several points, and 3) uniform or cross

flow ventilation, where each cell in series experiences a small but equal amount of inflow and outflow. Diagrams illustrating these ventilation patterns are provided in Figures 4.2.4(a) through 4.2.4(c).

The effects of these ventilation patterns were tested under four different scenarios. These hypothetical scenarios represented systems with low or high mass transfer coefficients, combined with low or high ventilation rates.

- Scenario 1 - Low mass transfer coefficient combined with low ventilation rate
- Scenario 2 - Low mass transfer coefficient combined with high ventilation rate
- Scenario 3 - High mass transfer coefficient combined with low ventilation rate
- Scenario 4 - High mass transfer coefficient combined with high ventilation rate

The specific mass transfer coefficients and ventilation rates which were employed are listed in Table 4.2.2. The low range of mass transfer coefficients were those which resulted from Equations 8 and 9 when they were used to estimate liquid-phase mass transfer coefficients for a 2.0 m diameter pipe flowing half-full along a 0.5% grade. The high range of mass transfer coefficients were those which resulted from Equations 8 and 9 when they were used to estimate liquid-phase mass transfer coefficients for a 0.5 m diameter sewer flowing one-fifth full along a 2.0% grade. Mass transfer coefficients for chloroform and trichloroethylene were the same because these two compounds are reported to have the same ψ values (Smith *et al.*, 1980). As in the previous modelling sections, ventilation rates represented exchanges of air over the entire reach. Thus, as the number of inlet and exhaust points increased, the air flow rate experienced along each individual air circuit decreased.

Figures 4.2.5 through 4.2.8 illustrate the results of this analysis. The CORAL model predicts that in the majority of scenarios overall mass removal is relatively insensitive to the spatial pattern of ventilation. In three of the four scenarios, changes in ventilation pattern resulted in less than a 6% change in overall mass removal for chloroform and in less than a 13% change in overall mass removal for trichloroethylene. However, in Scenario 2, mass removal under multiple cell inflow/outflow and uniform flow differed by 22% and 18% for chloroform and trichloroethylene, respectively. In the case of carbon tetrachloride, Scenarios 2, 3 and 4 involved differences in overall mass removal of less than 12%. However, in Scenario #1 mass removal under multiple cell inflow/outflow and uniform flow differed by 21%. The fact that the largest differences were observed under different scenarios is a result of different limitations which act on compounds of low and high volatility, as discussed in the previous section.

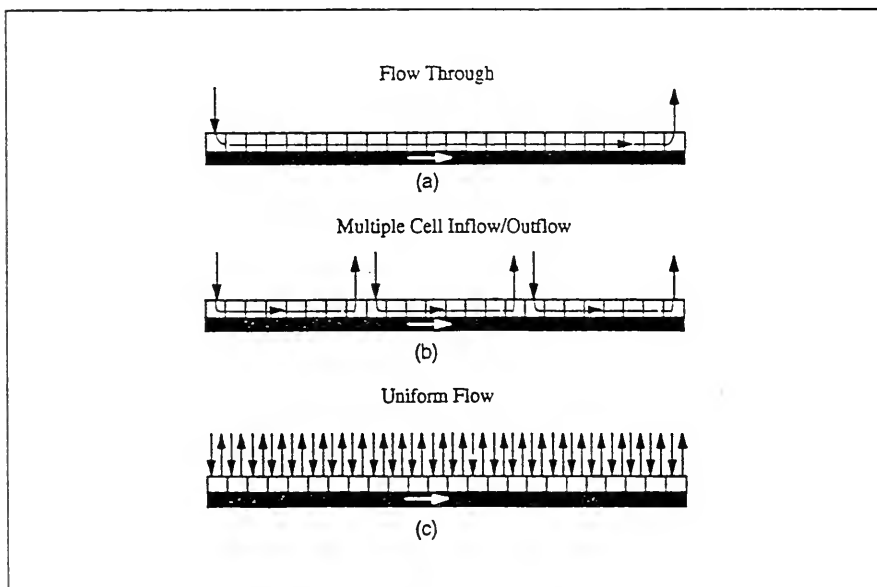


Figure 4.2.4 - Ventilation Patterns Simulated in this Study

Table 4.2.2 - Mass Transfer Coefficients and Ventilation Rates for Ventilation Pattern Analysis

Compound	Mass Transfer Coeff., K [1/hr]		Ventilation Rate [TuPD]	
	Low	High	Low	High
Chloroform	0.18	3.4	1.0	10.0
Trichloroethylene	0.18	3.4	1.0	10.0
Carbon Tetrachloride	0.20	3.8	1.0	10.0

Wastewater temperature = 20 °C, relative roughness coefficient = 0.014.

In the majority of cases, the largest discrepancy in overall mass removal was observed between multiple cell inflow/outflow and uniform flow patterns rather than between flow through and uniform flow. This was the result of different gas velocities and degrees of saturation that were present under the three spatial variations. Horizontal gas velocity was the highest for the flow through pattern, meaning that VOCs were swept quickly out of the reach. However, as the gas moved from the inlet to the exit, with no fresh intake of air, saturation of the headspace took place. Uniform flow represented the opposite extreme. There was no horizontal movement of air and, although there were many small intake and exhaust points, they did not produce the same effect. Although the overall system ventilation rate was the same, the residence time of air within each cell in the uniform flow pattern was fifty times longer than it was for the flow through pattern. Under these conditions, gas concentrations became elevated and the concentration driving force was diminished. This may explain why multiple cell inflow/outflow accomplishes the

Fractional Mass Removal vs. Ventilation Pattern
Scenario 1 - Low K, Low Vent.

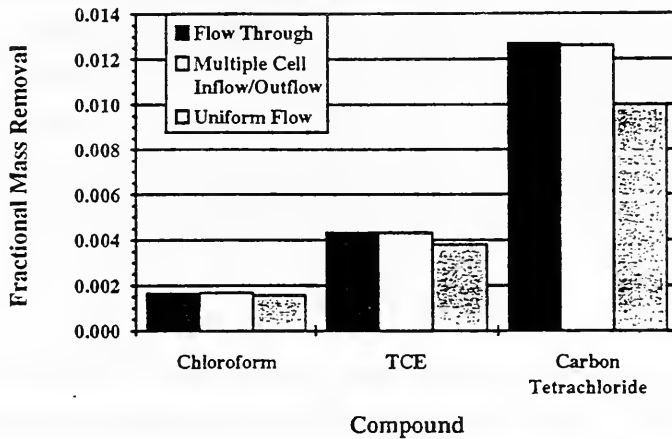


Figure 4.2.5 - Fractional Mass Removal vs. Ventilation Pattern for Scenario 1

Fractional Mass Removal vs. Ventilation Pattern
Scenario 2 - Low K, High Vent.

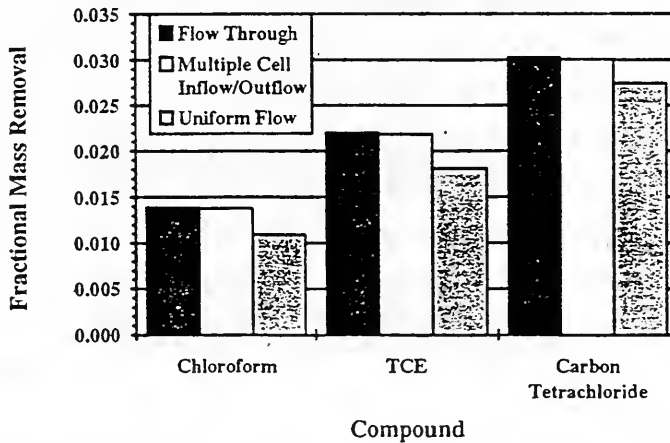


Figure 4.2.6 - Fractional Mass Removal vs. Ventilation Pattern for Scenario 2

Fractional Mass Removal vs. Ventilation Pattern for Carbon Tetrachloride
Scenario 3 - High K, Low Vent.

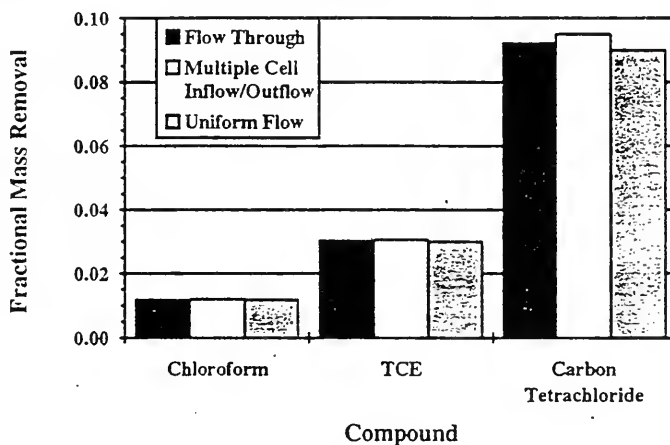


Figure 4.2.7 - Fractional Mass Removal vs. Ventilation Pattern for Scenario 3

Fractional Mass Removal vs. Ventilation Pattern for Carbon Tetrachloride
Scenario 4 - High K, High Vent.

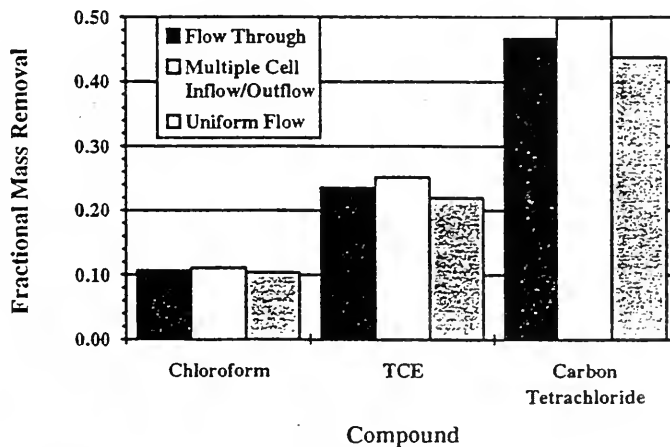


Figure 4.2.8 - Fractional Mass Removal vs. Ventilation Pattern for Scenario 4

greatest overall mass removal, under the majority of conditions tested. Although gas velocities under this spatial pattern were lower than those in flow through, the periodic fresh intakes of air did not allow the headspace to become saturated. It represented a compromise between the two extremes (flow through and uniform flow).

Over the thirty-six scenarios tested in this series of model simulations, the highest fractional mass removals were observed for the multiple cell inflow/outflow ventilation pattern, under Scenario 4, which combined high mass transfer coefficients with high ventilation rates. Fractional mass removals (mass removed from reach/total mass discharged to reach) of 0.11, 0.25, and 0.50 were predicted for chloroform, trichloroethylene and carbon tetrachloride, respectively. The lowest fractional removals were observed for uniform flow, under Scenario 1, which combined low mass transfer coefficients with low ventilation rates. Under these conditions, fractional mass removals of 0.0016, 0.0038, and 0.010 were predicted for chloroform, trichloroethylene and carbon tetrachloride, respectively. For Scenarios 2 and 3, fractional mass removals remained below 0.10. Therefore, as in the previous section, the relative magnitude of mass removal under the majority of scenarios was low (<10%).

4.3 Multi-Parameter Analysis

Multi-parameter analyses were completed using MATES (Multiparameter Assessment of Toxic Emissions from Sewers). The MATES model is an extension of CORAL (Corsi, 1992(a)). It uses the same computational solution to determine gas-liquid mass transfer and emissions along a sewer reach, but re-executes the model over user-specified ranges of input parameters. Results of these multi-parameter analyses were

presented at the 85th Annual Meeting of the Air and Waste Management Association. A copy of the conference paper has been included in Appendix C. Results for a 5 km reach may be summarized as follows:

- At relative depths greater than 0.3 and ventilation rates lower than 5 volume turnovers per day (TuPD), MATES predicted that 50% mass removal would never be achieved over the full range of diameters (0.3 - 2.1 m), slopes (0.05% - 4%), and Henry's law constants (0.1 - 1.1) considered.
- At relative depths of 0.1 and ventilation rates greater than 5 TuPD, MATES predicted 50% mass removal would occur in the majority of cases (65%). This points to a potential problem with the practice of off-hour industrial discharges, which are designed to take place when collection system flows are lowest.
- At absolute wastewater depths of greater than 0.4 m, 50% mass removal was never achieved, regardless of the pipe diameter. However, for absolute depths less than 0.4 m, the sensitivity of mass removal to depth of flow increased sharply.
- The degree of mass removal is highly sensitive to Henry's law constant at ventilation rates lower than 20 TuPD. However, this sensitivity to Henry's law constant disappears at higher ventilation rates, due to the diminishing value of C_g in Equation 1.

5.1 OVERVIEW

In addition to computational modelling, a number of field experiments were completed to broaden the understanding of gas-liquid mass transfer along sewer reaches. Specific objectives of this portion of the research were to design and conduct field experiments that would yield overall mass transfer coefficients for a wide range of sewer operating conditions, and to utilize data gained through the completion of these experiments to evaluate the gas-liquid mass transfer coefficient model (Equations 8 and 9) which forms an integral part of the CORAL fate/transport model.

Field experiments involved the injection of two volatile tracer compounds, deuterated chloroform (CDCl_3) and 1,1,1-trichloroethane (TCA), into the aqueous phase of a sewer reach, followed by measurement of steady-state gas and liquid phase concentrations downstream of the injection point. These results, combined with information regarding wastewater hydrodynamics, wastewater flow rate, and gas flow rate allowed the determination of an overall mass transfer coefficient for a given set of experimental conditions. Four experiments were completed at two field sites offering significantly different experimental conditions. These differing conditions were valuable in determining whether sensitivities observed while performing computational modelling are also observed in the field.

Field experiments have inherent difficulties, such as, lack of control over system variables, adverse weather conditions, and power and equipment limitations. Nevertheless, they were selected over laboratory or pilot-scale studies for several reasons.

These included the avoidance of existing uncertainties regarding sewer simulation and scale-up, and the extrapolation of clean water results to wastewater. It was also questionable as to whether or not adequate uniform reach length could be incorporated into a lab/pilot structure.

5.2 SITE DESCRIPTIONS

The two gravity sewers in which field experiments were completed were both located on the western boundary of the Guelph Wastewater Treatment Plant (GWWTP) (See Figure 5.2.1). The physical characteristics of each reach are listed in Table 5.2.1. The wastewater that was transported along Guelph Experimental Reach #1 was collected from the southwestern portion of the city and represented a mix of residential, commercial and light industrial discharges. The wastewater flowed under the Speed River in an inverted syphon and into a vented junction box. After travelling through the experimental reach, the wastewater traveled an additional 416 m to the wastewater treatment plant. The channel slope varied along the sewer reach but was constant between any two manholes. Between the junction box and the first manhole the slope was 0.15%. Between the first and second manholes the channel slope was 0.10%, and between the second and third manholes it was 0.08%. The piping was concrete and the walls exhibited little biological growth. The features which made this reach so suitable for experimentation were its shallow depth (from manhole cover to channel invert) of approximately 3.5 m, and its location, away from streets where sampling could affect normal traffic patterns and the safety of the research team.

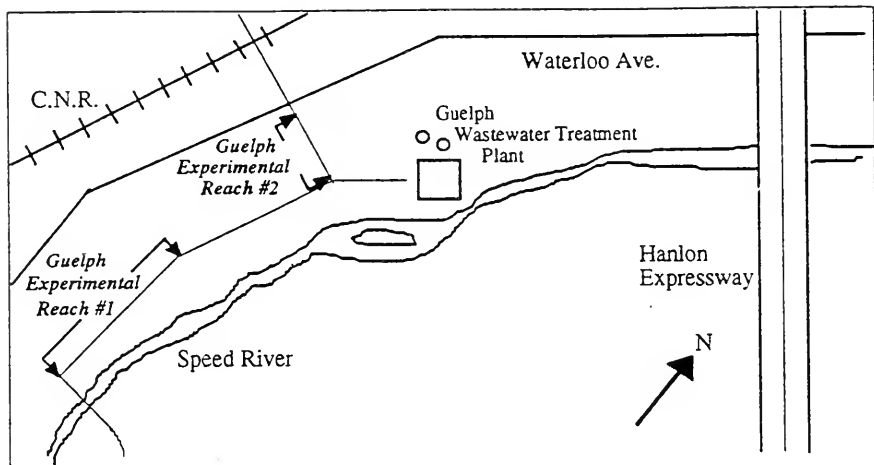


Figure 5.2.1 - Sketch Indicating Locations of Experimental Reaches (not to scale).

Table 5.2.1 - Physical Characteristics of Experimental Reaches

Experimental Reach	Pipe Diameter [m]	Pipe Composition	Reach Length [m]	Channel Slope [%]
Guelph #1	1.2	Concrete C-76-63-T Class III	122	0.10
Guelph #2	0.52	Concrete C-76-IV	64	3.5

Along Guelph #2, the piping was concrete (C-76-IV) and the walls exhibited little biological growth. The wastewater conveyed along this line was primarily residential, and was collected from the northwestern portion of the city. Although this line was far less suited to experimentation than Guelph #1, its 3.5 % channel slope provided an extreme test condition.

5.3 EXPERIMENTAL METHODOLOGY

The experimental system is illustrated in Figure 5.3.1, changes required to accommodate Guelph Experimental Reach #2 are described in Figure 5.3.2. Major components of the system included:

Ventilation System: A small blower was used to control gas flow in the experimental system and was located on the junction box which received wastewater from the aforementioned inverted syphon (at Guelph #1), or on Manhole #1 (at Guelph #2). The ventilation apparatus is described in detail in Section 5.3.2.

Sulfur Hexafluoride Injection and Collection: Sulfur hexafluoride (SF_6) was used to confirm gaseous flow rates in the sewer headspace. It was injected at Manhole #1 and collected at Manhole #2. The SF_6 tracer methodology is described in detail in Section 5.3.2.

Rhodamine Dye Injection and Collection: Rhodamine dye was used to characterize wastewater hydrodynamics and to quantify wastewater flow rate. It was injected at Manhole #1 and collected at Manhole #2. Rhodamine dye tracer methods are described in Section 5.3.1.

Volatile Tracer Injection and Collection: A cocktail of two volatile tracers was injected into wastewater at Manhole #1, with subsequent sampling in both wastewater and the overlying sewer headspace at Manhole #2. Methodologies associated with volatile tracer preparation, injection, sampling and analysis are described in Section 5.3.3.

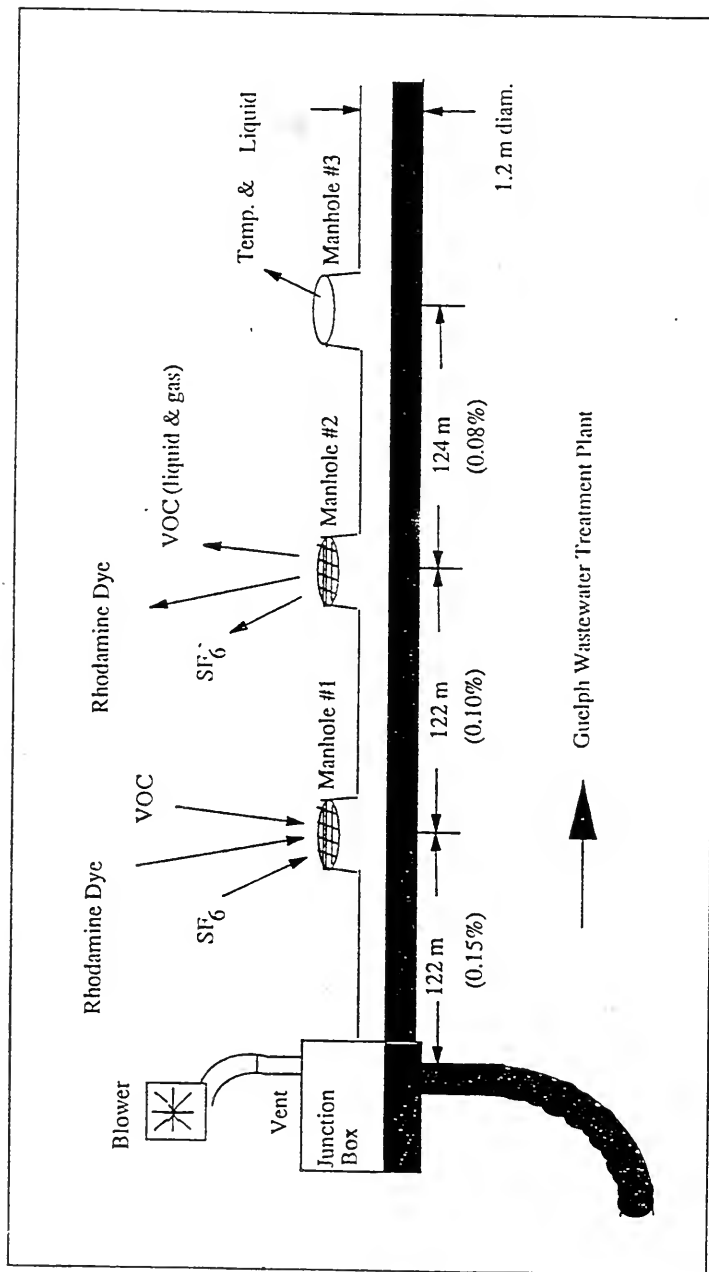


Figure 5.3.1 - Guelph Experimental Reach #1

Sample Collection to Determine Wastewater Characteristics: Wastewater characteristics were quantified following sample collection at Manhole #3, for experiments along Guelph #1, and at Manhole #2 for the experiment along Guelph #2. Characteristics which were monitored included temperature, pH, dissolved oxygen, conductivity and suspended solids. Analyses of these experimental conditions are described in Section 5.3.4.

Tracer concentrations coupled with wastewater and gas flow rates were used to back-calculate gas-liquid mass transfer coefficients for each system. The procedure used to complete input parameter estimation and perform these back-calculations is described in Section 5.3.5.

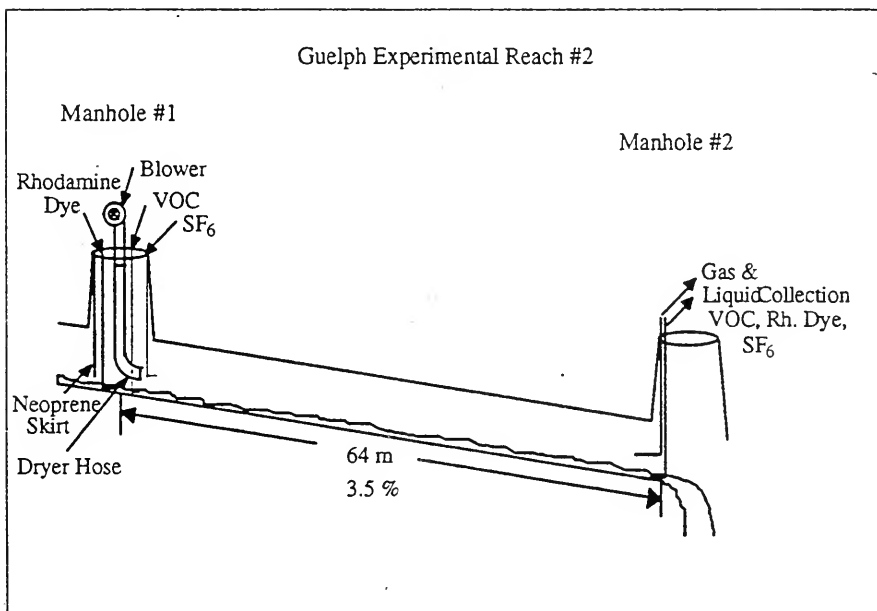


Figure 5.3.2 - Guelph Experimental Reach #2

From an experimental point of view, Guelph Experimental Reach #2 presented several difficulties. Only a small (64 m) portion of the reach was reasonably accessible. This meant that only two manholes were available for experimentation. Therefore, ventilation and injection took place at one manhole while collection and monitoring were coupled at the second manhole. In addition, no inverted syphon was present upstream to block potential air flow counter to the flow of wastewater. To overcome this problem, a neoprene skirt was hung at the most upstream point of the reach to block air flow, and the blower apparatus was modified to include a section of dryer hose containing a ninety degree bend. This elbow allowed air flow to be directed down the reach. Finally, the downstream collection manhole was also the location of a 0.5 m drop into an intersecting sewer reach. All collection lines, both gas and liquid, had to be inserted at least 0.3 m into the experimental reach in order to minimize any contribution to mass transfer by the drop.

5.3.1 System Hydrodynamics and Wastewater Flow Rates

RHODAMINE DYE TEST METHODOLOGY

As mentioned in the overview, information regarding sewer line hydrodynamics and wastewater flow rate had to be gathered during each experiment. Although numerous methods were considered, the dilution of an inert tracer dye was selected as both a practical and accurate alternative. Rhodamine dye (20% by weight) was obtained from Crompton and Knowles Inc., Montreal, P.Q.. Dilute rhodamine dye solutions were prepared prior to each experiment. Due to the volume of rhodamine dye required to carry out the testing, two separate batches were mixed for each experiment, one for testing system hydrodynamics, and one for determining wastewater flow rate.

The solution used for testing system hydrodynamics was prepared by drawing 50 mL of 20% rhodamine dye into a 50 ± 0.05 mL borosilicate glass pipette (ASTM Standard E969-83 Class A) and delivering this into a 2000 ± 0.50 mL PYREX volumetric flask, partially filled with deionized water. This flask was then filled to the mark with deionized water, covered with parafilm and thoroughly mixed. After mixing, the solution was transferred to two 1 L Nalgene polypropylene sample bottles.

The solution for testing wastewater flow rate was prepared by filling a 100 ± 0.08 mL PYREX volumetric flask with 20% rhodamine dye and transferring it to a 2000 ± 0.50 mL PYREX volumetric flask, partially filled with deionized water. The 100 mL flask was then rinsed three times with deionized water, with the contents of each rinse being added to the 2000 mL flask. After these rinses, the 2000 mL flask was filled to the mark with deionized water, covered with parafilm and thoroughly mixed. This solution was also transferred to 1 L Nalgene polypropylene sample bottles. All sample bottles were marked and stored at 4°C until needed.

Prior to beginning test runs, a rhodamine injection pump was calibrated using a stopwatch and 250 mL graduated cylinder. Two wastewater blanks were collected in 40 mL sample bottles. During the hydrodynamic portion of the test, rhodamine solution was pumped directly out of the 1 L sample bottles, into the wastewater, at Manhole #1 at a rate of 180 mL/min for 2 minutes. Forty wastewater samples were then collected, in 40 mL glass sample bottles, one manhole downstream of the injection port. Samples were capped with plastic screw-top caps and preserved in an ice chest during the remainder of the experiment. A second batch of the rhodamine dye was pumped into the wastewater, at Manhole #1, at a rate of 50 mL/min for 30 minutes to determine wastewater flow rate by dilution. Once 26 minutes had passed, the system had achieved steady state and four 40 mL sample bottles were filled, one manhole downstream of the injection point, at one

minute intervals. These samples were also placed in the ice chest. Polyethylene tubing (6.5mm OD) and a 600 rpm peristaltic pump (Cole-Parmer Model # 7553-20) were used for both injection and collection. Upon return to the laboratory, all rhodamine samples were transferred from the ice chest to a refrigerator and kept at 4 °C.

RHODAMINE DYE STANDARDS

Approximately 20 mL of rhodamine dye (20% by weight) was delivered to a 50 mL beaker. A stock solution of suitable concentration, 10.3 mg/L, was made through a two step serial dilution. This involved drawing 5.0 mL of rhodamine dye into a Hamilton gas-tight syringe (#1005) and delivering it into a 1000 +/- 0.30 mL PYREX volumetric flask, partially filled with deionized water. This volumetric flask was then filled to the mark with more deionized water, covered with parafilm, and thoroughly mixed by hand. A portion of this new solution was delivered into a 250 mL Erlenmeyer flask and 5.0 mL were again drawn into a clean Hamilton gas-tight syringe (#1005), and delivered into a 500 +/- 0.20 mL PYREX volumetric flask, partially filled with deionized water. This volumetric flask was then filled to the mark with more deionized water, covered with parafilm and thoroughly mixed by hand. A portion of this stock solution was delivered to a 50 mL Erlenmeyer flask and the remainder stored in a capped glass sample bottle and stored at 4 °C for future use.

The portion of the stock solution delivered to the Erlenmeyer flask was used in variable-volume formulation of standards. A 5.0 mL Hamilton gas-tight syringe (#1005) was used to deliver 2.5 mL of stock solution into a partially filled 50 mL +/- 0.20 mL PYREX volumetric flask. The flask was then filled to the mark with deionized water, covered with parafilm and thoroughly mixed by hand. This yielded a standard rhodamine

dye solution of 515 ppb. Additional standards of 206 ppb, 103 ppb, 51.5 ppb, and 20.6 ppb were made in 50 mL \pm 0.20 mL volumetric flasks by drawing and delivering 1.0 mL and 500 μ L of stock solution with a 1000 μ L Hamilton gas-tight syringe (#1001), and 250 μ L and 100 μ L of stock solution with a 250 μ L Hamilton gas-tight syringe (#1725). All flasks were filled with deionized water, covered with parafilm and thoroughly mixed by hand. Standards were stored at 4 $^{\circ}$ C for future use.

RHODAMINE DYE ANALYSIS

Rhodamine dye analysis took place not more than 48 hours after each experiment was completed. A Turner Model #430 spectrofluorometer was used. Rhodamine dye standards were examined at the beginning of each series of analyses to produce a calibration curve. Curves were based on four calibration points with coefficients of determination (R^2) ranging from 0.98 to 0.99, over the four experiments. Calibration curves for each experiment are provided in Appendix A. Wastewater blanks collected at the beginning of each experiment were utilized to judge the baseline fluorescence of the wastewater prior to the addition of rhodamine dye. This baseline fluorescence was subtracted from subsequent rhodamine samples, so that only the fluorescent contribution of the rhodamine-dye was considered. Finally, all wastewater samples collected during rhodamine dye injection were analyzed. The results of all rhodamine dye analyses are provided in Appendix B.

As rhodamine standards were prepared with distilled water and not with wastewater, a small test was performed to ensure that this would not introduce significant error into the analysis of rhodamine samples. Identical rhodamine dye standards were prepared in distilled water and in fresh unfiltered wastewater. Analysis of these two sets of standards showed that quenching effects of the wastewater varied with rhodamine dye

concentration but resulted in an average 9% decrease in spectrofluorometer readings. In light of the variable quenching effects, rhodamine sample readings were not adjusted. Without adjustment, rhodamine sample readings underestimated actual concentrations and thus resulted in slightly overestimated wastewater flow rates.

5.3.2 Sewer Reach Ventilation

VENTILATION APPARATUS

The reaches in which tracer experiments were carried out were force ventilated using a small blower apparatus powered by a portable generator. This ventilation accomplished two objectives. It provided constant ventilation throughout the duration of an experiment, and also accelerated the rate at which steady-state conditions were achieved.

Two different blowers were used depending on the desired ventilation rate (Figures 5.3.2 (a) and (b)). The smaller blower was comprised of a 15 cm fan and cage, powered by a 3000 rpm motor. This blower had a circular 5.5 cm outlet which was fixed to a 5.5 cm ID PVC pipe, 63 cm in length. The second blower consisted of a 10.5 cm fan and cage, and was powered by a 3400 rpm motor. Wooden plates (22.5 cm diameter) were sealed around the outlets of each blower. This allowed the blowers to be interchangeably mounted on a sheet metal stack 22.5 cm in diameter and 61 cm in length. This stack provided an outer shell that could be slipped over the 22.5 cm diameter vent on the sewer line junction box. A small 1.5 cm hole tapped in the PVC pipe and a slightly larger 2 cm hole was punched out of the sheet metal wall, and provided access to the air flow such that a hot wire anemometer (Air Flow Developments Canada, Model #TA6000)

could be used to measure air velocity. After each flow measurement was made, these holes were closed with a tapered plug and duct tape.

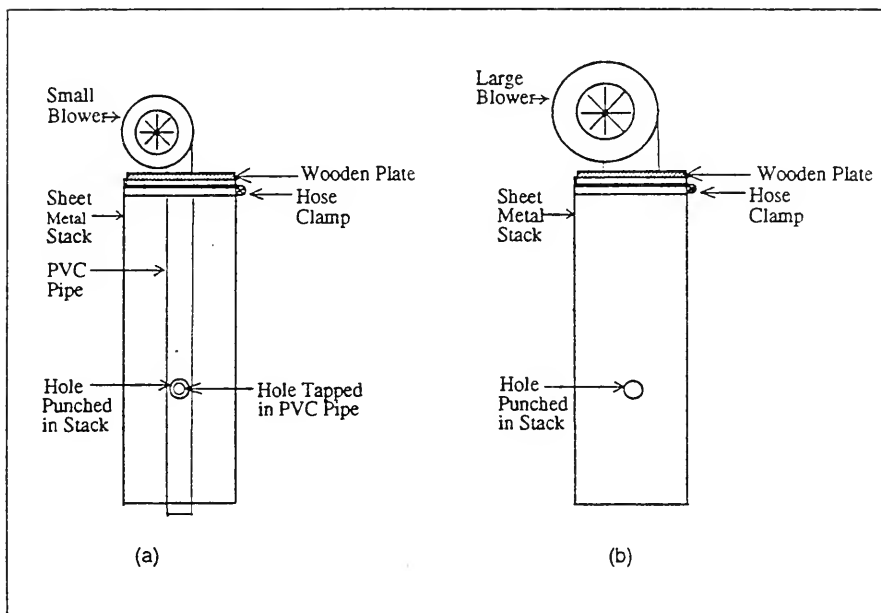


Figure 5.3.2.1 - Blower apparatus used to ventilate experimental reaches (a) with small blower in place, (b) with larger blower in place.

SULFUR HEXAFLUORIDE TEST METHODOLOGY

Although each experimental sewer reach was force ventilated at a constant rate by a blower of known capacity, it was decided that a more accurate and reliable means of determining sewer gas flow rate should be incorporated into each experiment. As such, a small amount of sulfur hexafluoride (SF_6) was introduced at Manhole #1 and dilute downstream gas samples were collected at Manhole #2. A 40 L Tedlar® bag was filled

with sulfur hexafluoride (99.8% purity), from a 3.18 kg (7 lb) cylinder, and transported to the field. An air sample pump (SKC Airchek Sampler Model #224-PCXR7) with a single port manifold (SKC Part # 224-26-01) and 6.5 mm OD polyethylene tubing were used to inject the sulfur hexafluoride into the headspace of the sewer reach, approximately 6 cm above the surface of the wastewater.

The system was allowed to come to steady state. Preliminary calculations had shown that, for the first two experiments, one complete change of air would be completed in approximately 30 minutes. For these two experiments, 90 minutes were allowed for the system to come to steady state. For the third and fourth experiments, greater ventilation rates meant that complete changes of air would be accomplished in 10 and 5 minutes, respectively. For these two experiments 30 minutes and 15 minutes were allowed for the systems to reach steady state. Throughout the period of injection, manhole covers remained in place with pickholes sealed. An air sample pump (SKC Airchek Sampler Model #224-PCXR7) and 6.5 mm OD polyethylene tubing were used to draw headspace gas, at a rate of 2.5 L per minute, one manhole downstream of the injection port. A plastic T-connection within the line allowed the collection of five gas samples using sterile 10 mL plastic surgical syringes with PVC Luer-lok stopcocks. An ambient air sample was also drawn.

SULFUR HEXAFLUORIDE STANDARDS AND ANALYSIS

A sulfur hexafluoride "stock" standard was used for preparing sulfur hexafluoride calibration curves. This standard was prepared in a 60 mL plastic surgical syringe fitted with a PVC Luer-lok stopcock. The sterile syringe was filled with 50 mL of charcoal polished ultra high purity nitrogen gas. Ten microliters of sulfur hexafluoride (99.8%

purity) were then injected through the stopcock using a 10 μ L gas-tight syringe (Hamilton #1701RN). This yielded a standard of 1.32 μ g SF₆/L.

Analyses of the experimental gas samples were completed using a Hewlett Packard Gas Chromatograph with an Electron Capture Detector (GC/ECD HP 5890 Series II). At the beginning of each analysis, 2, 4 and 5 μ L volumes were drawn from the SF₆ standard using a 10 μ L gas-tight syringe (Hamilton #1701RN). These were directly injected onto the chromatographic column (J & W Scientific # 123-5033, 30m x 0.32 mm ID, Phase DB5, Film Thickness 1.0 micron). Injector, GC oven, and detector temperatures were 200 $^{\circ}$ C, 35 $^{\circ}$ C, and 250 $^{\circ}$ C, respectively, and the column flow rate was 1.5 mL/min. The resulting calibration curves exhibited R² values ranging from 0.98 to 0.99 and are provided in Appendix A. All gas samples were then analyzed by drawing 10 μ L of air from each sample syringe and directly injecting it into the GC/ECD. The syringe was cleaned between samples using a heated and evacuated syringe cleaner. The ambient air sample was utilized to judge the baseline response of the ambient atmosphere. The results of these sulfur hexafluoride analyses are provided in Appendix B.

5.3.3 VOC Tracer Compounds

VOC TRACER SOLUTION

Two volatile organic compounds, deuterated chloroform (CDCl₃, 99.8% atom D), obtained from MSD ISOTOPES, Montreal, P.Q., and 1,1,1-trichloroethane (TCA, 96.5%), obtained from Fisher Scientific Ltd., Toronto, Ont., were used as tracers during field experiments. These compounds were selected because they satisfied several key criteria. They represented two of the eleven target compounds identified for review during this research project by the Ontario Ministry of the Environment. They exhibit low

(CDCl_3) and high (TCA) Henry's law constants relative to the other 11 target compounds, and both were predicted to have little affinity for adsorption, according to a model for sorption developed by Dobbs (1989). In addition, previous monitoring events indicated that little or none of these compounds were present in Guelph wastewater. The physicochemical properties of each tracer are listed in Table 5.3.1.

Table 5.3.1 - Physicochemical Properties of Experimental Tracer Compounds

Compound	Molecular Weight [amu]	Solubility @ 25 °C [†] [mg/L]	$\log_{10} K_{ow}$ [†]	Henry's Law Constant [‡] @ 20 °C [-]
Chloroform-d	120.4	7950	1.97	0.12
1,1,1-Trichloroethane	133.4	1495	2.49	0.60

[†] Handbook of Environmental Fate and Exposure Data for Organic Chemicals, 1990.

[‡] Using relationships derived by Gossett, 1987.

Preparation of the VOC tracer solutions demanded attention to physical and experimental constraints. Tracer compounds were kept at levels at least three times below their solubility in water. In addition, it was desired that the total solution volume be kept below 24 L, a volume which could be reasonably transported to the field. Finally, it was necessary that the solution, combined with its injection rate, yield liquid and gas-phase sample masses that were above the detection limit and within the linear response range of the analytical equipment used to quantify them. These masses ranged from approximately 0.05 to 1.5 µg. Sample volumes were also adjusted to bring the masses into this range. In this case, the gas-liquid mass transfer model CORAL was utilized to predict gas-phase concentrations, given known liquid mass flow rates and approximate reach operating characteristics. Consideration of all of these factors meant that different solution concentrations and/or injection rates were employed for each experiment. Over the course of the four experiments, target solution concentrations ranged from 312 to 625 mg/L for

deuterated chloroform and from 279 to 558 mg/L for 1,1,1-trichloroethane. As noted in Table 5.3.1, solubilities of deuterated chloroform and 1,1,1-trichloroethane in water at 25°C are 7950 mg/L and 1495 mg/L, respectively. Injection rates for each experiment are provided in Table 5.4.5.

In preparing for each experiment, predetermined volumes of tracer compounds were drawn into 10 mL glass syringes and delivered into a 100 mL +/- 0.08 mL PYREX volumetric flask partially filled with methanol. The flask was then filled to the mark with methanol and capped. Meanwhile, a 40 L Tedlar® bag was filled with 23.8 L of tap water using a 6-600 rpm peristaltic pump (Cole-Parmer Model # 7553-20), and 6.5 mm OD polyethylene tubing. The volume delivered to the bag was controlled by pumping out of a 12L glass carboy filled multiple times using 2 L, 1 L, 500 mL, 250 mL, 100 mL, and 50 mL volumetric flasks, such that a total of 23.8 L were delivered.

After the Tedlar® bag had been filled with water, the methanol solution containing the selected tracers was quickly pumped into the bag using the same pump but switching to FEP Teflon® tubing. The volumetric flask was flushed with an additional 100 mL of methanol, which was also pumped into the bag. Twelve hours were allowed between bag filling and experiments in order to ensure that complete dissolution of both tracer compounds had taken place.

VOC TRACER INJECTION AND COLLECTION

A Tedlar® bag containing the VOC tracer solution was transported to the field in a plastic tray. Once located at the injection station, the bag was covered with an opaque tarp to minimize any possibility of photochemical reaction. Prior to injection of VOC

tracer, two wastewater blank samples were collected and stored in 40 mL amber/borosilicate vials, capped with 3 mm Teflon® fluorocarbon resin silicone septa (Precleaned to EPA Protocol B Cleaning Standards). The tracer solution was then pumped from the Tedlar® bag into the wastewater using 6.5 mm OD FEP Teflon® tubing and a 6-600 rpm peristaltic pump (Cole-Parmer Model #7553-20), calibrated to deliver a specific flow rate dependent upon experimental conditions. The Tedlar® bag collapsed as it was evacuated, ensuring that no headspace developed over the injection period.

Running the CORAL sewer model prior to commencing the experiments allowed estimation of the time required to reach steady state. Once this time had been reached in the field, both gas and liquid samples were collected at Manhole #2. Wastewater was pumped to the surface using 6.5 mm OD FEP Teflon® tubing and a 6-600 rpm peristaltic pump (Cole-Parmer Model # 7553-20). Four liquid samples were collected in 40 mL amber/borosilicate vials. Collection was accomplished with as little agitation as possible and no headspace was permitted in the capped vials. All liquid samples were immediately stored in an ice chest.

Sewer gas was pumped to the surface using 6.5 mm OD FEP Teflon® tubing and an air sample pump (SKC Airchek Sampler Model # 224-PCXR7) equipped with a single port manifold (SKC Part # 224-26-01). Five gas samples were collected on 6.5 mm OD stainless steel sorbent tubes (Carbotrap™ 300 Multi-bed Thermal Desorption Tubes) sequentially packed with two graphitized carbon black adsorbent beds (Carbotrap C and Carbotrap), and a spherical carbon molecular sieve (Carbosieve™). All tubes were conditioned, 12 hours prior to each experiment, in a Tekmar® Multi-Tube Conditioner, at 280°C for 3 hours with a stream of charcoal polished ultra-high purity nitrogen set to 30-50 mL/min per tube.

In the field, gas flow rates through the tubes were monitored using a digital bubble flow meter (Hewlett Packard #9301-1231). Following gas collection, each tube was sealed using Teflon® ferrules and stainless steel Swagelok® plugs at both ends. All gas samples were immediately stored in a hermetically-sealed glass container and kept in an ice chest. Upon return to the laboratory, VOC samples were transferred to a refrigerator maintained at 4°C.

Several additional adsorbent tubes were also included amongst the VOC samples. These included a field blank, a breakthrough tube and a trip spike. The trip spike was intended to provide an indication of the recovery of VOC tracers from the adsorbent tubes. It was prepared 12 hours prior to each experiment in a manner identical to that described for VOC standards in the next section. A known amount of a standard mixture was purged onto the tube. It was then sealed using Teflon® ferrules and stainless steel Swagelok® plugs and stored in a hermetically-sealed glass container. The tube was transported to the field, remained unopened throughout the experiment, and was then analyzed with the rest of the gas samples upon return to the laboratory.

The field blank was utilized to identify any background contamination of tubes with CDCl_3 or TCA present in the ambient experimental atmosphere. It was a conditioned adsorbent tube that was opened at the beginning of gas sampling, and placed on the sealed manhole cover for the duration of VOC sampling. It was also sealed using Teflon® ferrules and stainless steel Swagelok® plugs and stored in a hermetically-sealed glass container. The breakthrough tube provided assurance that breakthrough had not occurred during the collection of gas samples. It was a conditioned adsorbent tube that was attached, in series, to the back of one of the VOC gas sampling tubes during collection of sewer gas samples. It was sealed using Teflon® ferrules and stainless steel Swagelok® plugs and stored in a hermetically-sealed glass container. Field blank and

breakthrough tubes were analyzed with the rest of the gas samples upon return to the laboratory.

VOC STANDARDS AND ANALYSIS

Purgeable mixtures containing known quantities of deuterated chloroform, 1,1,1-trichloroethane, toluene and ethylene dibromide in methanol were used in the preparation of standard curves. Although toluene and ethylene dibromide were not relevant to this study, they were required for a parallel study conducted by another researcher. These standard mixtures were prepared using three-step serial dilution. First, a 1 mL borosilicate vial was filled with 960 μL of methanol, using a 1 mL syringe with graduations of 50 μL . Then, 10 μL of each of the compounds was added to the vial using a 10 μL syringe. This yielded a solution containing 10 $\mu\text{L}/\text{mL}$ of each of the four compounds. Three serial, 1:10 dilutions were completed by adding 100 μL of each preceding solution to a 1 mL borosilicate vial containing 900 μL of methanol. Resulting mixture concentrations were 0.01 μL , 0.1 μL and 1.0 μL of each compound per millilitre of methanol.

Following each experiment, calibration curves were prepared for deuterated chloroform and 1,1,1-trichloroethane by purging various volumes of standard solutions onto Carbotrap 300 adsorbent tubes using a sealed purging vessel and charcoal-polished, ultra-pure nitrogen as the purge gas (See Figure 5.3.4). Standards were drawn into a 10 μL syringe (Hamilton #1701) and then injected through a Teflon® septum fitted to the side arm of the purging vessel. A water-bath surrounding the purging vessel was maintained at 60°C, and at least 1 L of nitrogen was purged through each tube at a rate of approximately 100 mL/min. Resulting calibration curves exhibited R^2 values ranging from 0.92 to 0.99 and are provided in Appendix A.

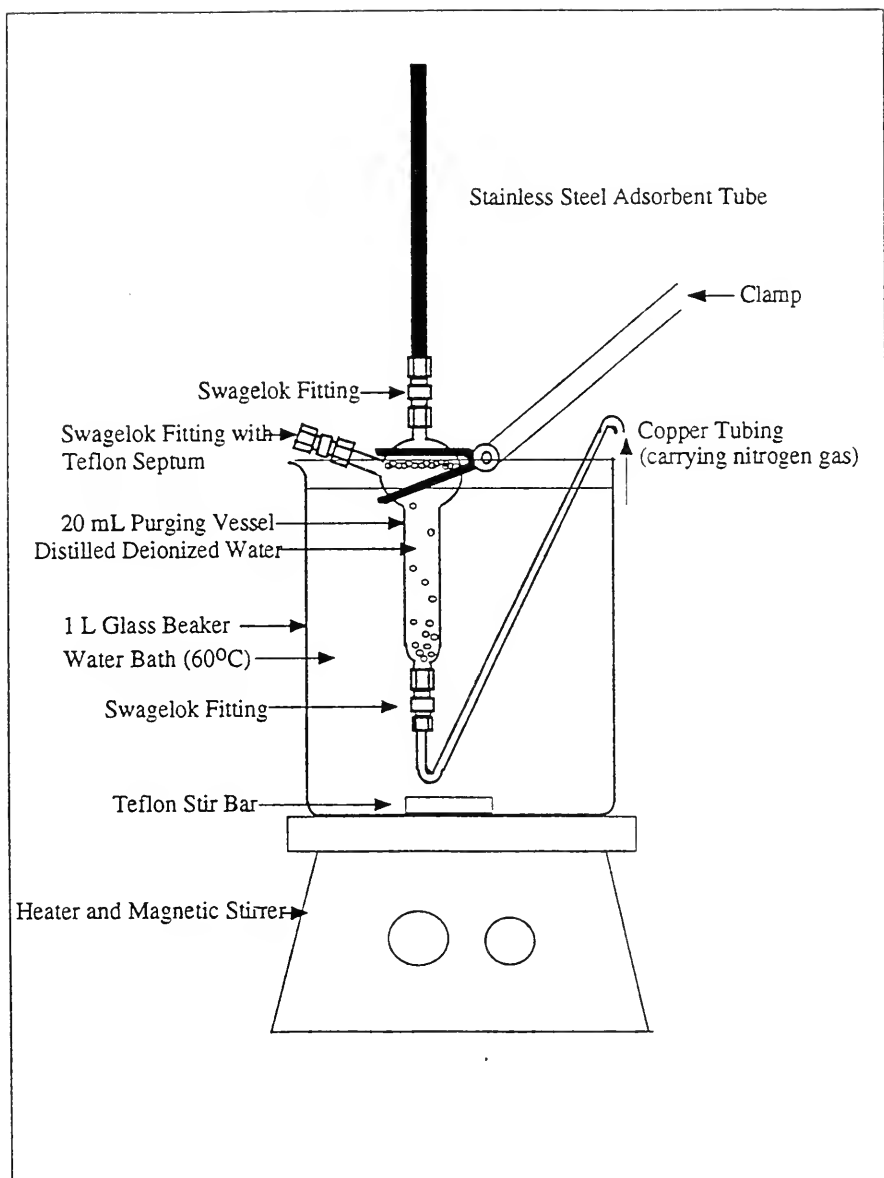


Figure 5.3.4 - Purging Vessel Setup

Stored gas and liquid samples were removed from the refrigerator and allowed to come to room temperature. Gas samples required no further preparation. In the case of wastewater samples, 10 mL were first purged with charcoal-polished, ultra-pure nitrogen onto a Carbotrap 300 adsorbent tube, which was then analyzed via the same methodology as gas samples. This purging procedure took place in the same water-bath (60°C) used to prepare VOC standards, however, the vessel was exchanged for a vessel reserved for the purging of wastewater samples. Samples were purged with at least 1 L of charcoal-polished, ultra-pure nitrogen at a rate of approximately 50 mL/min. The purging gas flow rate was lowered in order to reduce sample foaming. A small quantity of glass wool was inserted into the neck of the purging vessel to prevent foam from migrating into the sorbent tubes. A 10 mL glass syringe equipped with a Teflon Luer-lok fitting and approximately 9 cm of 3.2 mm ID Teflon tubing was used to deliver and remove wastewater from the vessel. Insertion of this tubing into the arm, and down to the bottom of the vessel eliminated agitation of the wastewater as it was fed into the vessel and allowed the used wastewater to be collected after purging.

A Tekmar® LSC 2000 purge and trap (PAT) thermal desorption unit interfaced with a Hewlett Packard 5890 Series II Gas Chromatograph and a Hewlett Packard 5971 Mass Selective Detector (quadrupole mass spectrometer) were used in analyzing all VOC standards and samples. Adsorbent tubes were mounted, one at a time, in place of the normal PAT internal Tenax trap. Tubes were dry purged for 2.50 minutes with a 60 mL/min stream of charcoal-polished, ultra high purity helium. Desorption then took place at 190°C for 2.75 minutes, followed by a bake at 260°C for 2.00 minutes.

The gas chromatograph (GC) was equipped with a DB-5 30 m x 0.20 mm ID capillary column with a 1.0 micron film thickness. Desorbed analytes were condensed at

the head of the column at room temperature (approximately 25°C). The GC oven was programmed to ramp at 30 °C/min to 39 °C where it was held for 2.20 minutes (solvent delay). This was followed by a 9 °C/min ramp to 150 °C, and a 30 °C/min ramp to 210 °C where the column was held for 2.00 minutes.

The mass spectrometer (MS) transfer line was maintained at 280°C. The MS was set to scan all ions from m/e 25 to m/e 250, at approximately 2 cycles/s. Data acquisition began after the solvent delay and continued until the end of the GC run.

5.3.4 Experimental Conditions

General physical and chemical measurements were obtained as a means of characterizing the environmental conditions during each experiment. Some measurements such as wastewater temperature, pH, and dissolved oxygen concentration, were recorded directly, while others such as total suspended solids and total organic carbon required the collection of wastewater samples, and subsequent laboratory analysis.

TEMPERATURE, pH, CONDUCTIVITY AND DISSOLVED OXYGEN MEASUREMENTS

Several temperature measurements were obtained during each experiment. Ambient air temperature was obtained using a standard mercury thermometer (Fisher #15-000A) with a range of -10°C to 51°C and graduations of 0.1°C. Wastewater temperature and sewer air temperature were measured using a dissolved oxygen (DO) meter (YSI Model # 58) and standard field sampling probe (Model #5740). Sewer air temperature readings were approximately 5 cm above the surface of the wastewater. One ambient air

temperature reading and two wastewater and sewer air temperature readings were obtained over the course of each experiment.

Dissolved oxygen measurements were obtained using a DO meter (YSI Model # 58) and standard field sampling probe (Model #5740). With Guelph Experimental Reach #1, it was possible to lower the probe into the flowing wastewater. With Guelph Experimental Reach #2 it was necessary to first pump the wastewater sample into a 1 L Nalgene sample bottle and then obtain a DO measurement. Two DO measurements were made during each experiment completed along Guelph Experimental Reach #1 and one DO measurement was obtained during the experiment completed along Guelph Experimental reach #2.

Conductivity and pH measurements were made using portable conductivity (Hanna Instruments HI 8033) and pH meters (Cole-Parmer 3 Function Chem-Cadet Model #5850-00). The conductivity meter was calibrated in the laboratory with a prepared 10,000 micromho solution obtained from the manufacturer. The pH meter was calibrated in the field using standard buffer solutions for pH 7 and 10. The field probes available for these instruments were not long enough to be lowered into the wastewater. Therefore, a 0.75 L Nalgene cup (10 cm diam. mouth) fixed to the end of a 3 m, 1.5 cm square bar was used to obtain a wastewater sample, from which both conductivity and pH measurements were made. Again, with Guelph #2, conductivity and pH readings had to be taken from the wastewater sample which had been pumped to the surface. One pH and one conductivity measurement were obtained for each experiment. A table summarizing temperature, pH, conductivity and DO results is provided in Appendix B.

TOTAL SUSPENDED SOLIDS AND TOTAL ORGANIC CARBON ANALYSIS

For the purposes of determining total suspended solids (TSS) and total organic carbon (TOC) concentrations, clean 1 L Nalgene bottles were filled using the Nalgene cup ladle described in the previous section. Bottles were labelled, and transferred to an ice chest. Upon return to the laboratory, all samples were transferred to a refrigerator and kept at 4°C.

For TSS analysis at least 2 samples were collected and duplicate analyses were completed on each sample, ie. two separate sub-samples were obtained from each wastewater sample and analyzed. Total suspended solids analysis was performed according to Method 2540D of the Standard Methods Handbook for the Examination of Water and Wastewater (17th Ed.). Glass fibre filters (Whatman 934-AH) and aluminum sample trays were used. Results of all TSS analyses are provided in Appendix B.

Total organic carbon analyses were performed by a commercial laboratory (Canviro Analytical Laboratories Ltd.). Due to cost constraints, TOC samples were only collected during one of the four experiments. Four samples were transported to the commercial laboratory in an ice chest. They were preserved and then analyzed. Results were forwarded in a written report. A copy of the report is provided in Appendix B.

5.3.5 Back-Calculation of Experimental Mass Transfer Coefficients

Back-calculation of experimental mass transfer coefficients was accomplished by iteration using the CORAL model. This model required numerous input parameters including:

1. Characteristics of the reach (length, pipe diameter, slope, and relative roughness)
2. Wastewater temperature
3. Ventilation rate
4. Wastewater depth
5. Number of CFSTRs in series that should be used for modelling the reach
6. Initial conditions (gas and liquid phases)
7. Manner in which the compound of interest was discharged (boundary condition)
8. Concentration of compound which was discharged
9. VOC of interest
10. Estimated mass transfer coefficient (for iteration purposes)

Pipe diameter, channel slope, relative roughness and wastewater depth, were used by the model to determine wastewater flow rate using Manning's Equation and wastewater temperature was used to determine Henry's law constants for the specified compounds using relationships derived by Gossett (1987). This information was then used in conjunction with the number of reactors (CFSTRs in series), ventilation rate, initial conditions, boundary conditions and mass transfer coefficient to model VOC gas and liquid concentration profiles along the sewer reach, as a function of time.

Input parameters for each model run were determined from engineering drawings, or estimated from experimental data collected over the course of each experiment. Reach length, pipe diameter, and channel slope were obtained from engineering drawings of the experimental reaches. Wastewater temperature was equated to the average of temperature measurements obtained during the course of the experiment. Ventilation rates were estimated based on dilution of sulfur hexafluoride gas.

As the dilution of rhodamine dye was used to calculate wastewater flow rate, model iterations were run at several wastewater depths, until the model's calculated wastewater flow rate matched the measured wastewater flow rate. Rhodamine dye slug injections were used to determine system hydrodynamics by selecting the number of CFSTRs which best simulated the measured dispersion of a rhodamine dye slug along the sewer reach.

Initial concentrations of volatile tracers were assumed to be negligible in both the gas and liquid phases. Tracer discharge was estimated to be constant and instantaneously mixed in the flowing wastewater. Discharged VOC concentrations were estimated to be equal to measure VOC liquid concentrations.

Finally, model iterations were completed for each tracer compound, using best-estimates of mass transfer coefficients. Estimates were adjusted until such time as the model's predicted steady-state gas-concentration at the end of the sewer reach matched the experimentally measured tracer gas concentration. This "back-calculated" mass transfer coefficient was then recorded as the experimental mass transfer coefficient.

5.4 EXPERIMENTAL RESULTS & DISCUSSION

A total of four field experiments were completed from May 1992 to July 1992. Three experiments (Experiment 1.1, 1.2, and 1.3) were completed along Guelph Experimental Reach #1 and one experiment (Experiment 2.1) was completed along Guelph Experimental Reach #2. The results of these experiments are presented and discussed in the following sections.

5.4.1 System Hydrodynamics and Wastewater Flow Rates

The results of system hydrodynamics tests were plotted for each experiment. Computational simulations were then completed to determine whether the dispersion exhibited by the sewer reach was characteristic of a well-mixed or plug-flow system, and to determine what number of CFSTRs was most appropriate to characterize wastewater hydrodynamics. Within these simulations, the injected rhodamine dye was assumed to instantaneously mix with the flowing wastewater. By taking the mass injection rate of rhodamine dye and the wastewater flow rate as determined for each experiment, an ideal slug concentration was calculated. A two-minute injection of this ideal concentration was modelled under different hydrodynamic conditions (1, 10, 50, 100, 150, and 200 CFSTRs). In matching experimental and predicted results, both the concentration profile and the duration of the slug were taken into account. The results of several trial runs indicated that the experimental reaches exhibited plug-flow behaviour, which was best simulated by at least 200 CFSTRs in series. Results for 100, 150 and 200 CFSTRs in series were nearly identical, as ideal plug-flow conditions were approached. Additional model runs, placing more CFSTRs in series would not have improved the fit between experimental and predicted results. Differences in experimental versus modelled profiles

may be attributed to wastewater quenching of rhodamine dye samples, as noted in Section 5.3.1. Figure 5.4.1 shows the concentration profile measured during Experiment 1.3, as well as the predicted concentration profiles for the reach when modelled as 10, 50, and 200 CFSTRs in series.

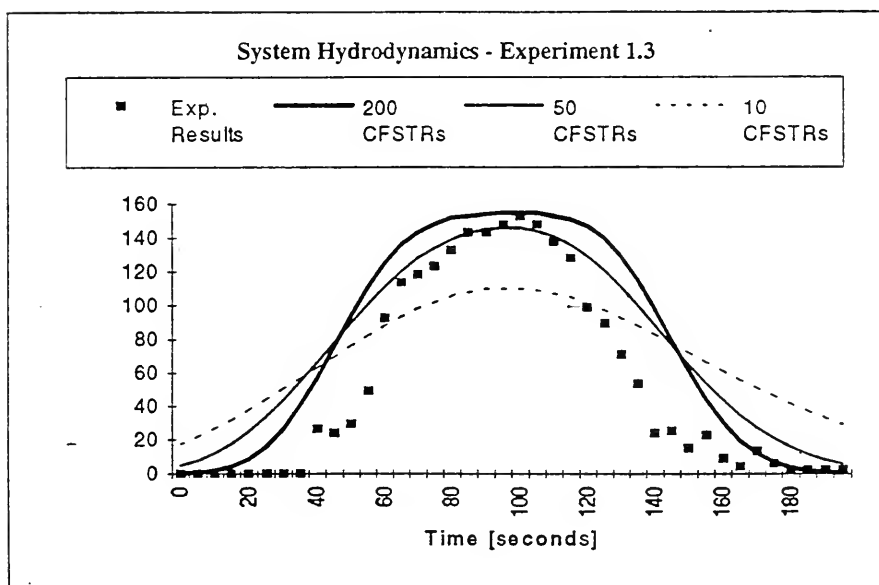


Figure 5.4.1 - System hydrodynamics for Experiment 1.3.

Wastewater flow rates were determined by dilution of rhodamine dye, with samples collected during steady state conditions. Table 5.4.1 provides a summary of wastewater flow rates, wastewater velocities and relative depths for each experiment. The relative depths have been calculated using Manning's Equation for circular channels, and an assumed relative roughness coefficient of 0.014. Wastewater flow rates for Guelph #1 ranged from 0.071 to 0.17 m³/s. The wastewater flow rate for Guelph #2 was 0.020 m³/s.

Wastewater velocities along Guelph #1 ranged from 0.56 m/s to 0.72 m/s. These velocities are typical of the velocities observed in many sanitary sewer systems. The 1.5 m/s wastewater velocity observed along Guelph #2, on the other hand, is somewhat high, and is a result of the reach's steep slope.

Table 5.4.1 - Wastewater Flow Conditions

Experiment	Wastewater Flow Rate [m ³ /s]	Wastewater Mean Velocity [m/s]	Relative Depth [-]
1.1	0.17	0.72	0.25
1.2	0.071	0.56	0.17
1.3	0.10	0.62	0.19
2.1	0.020	1.5	0.11

5.4.2 Gas Flow Rates

Sewer gas flow rates were determined by dilution of sulfur hexafluoride gas. Gas flow rates were also estimated using gas velocity measurements obtained with a hot wire anemometer immediately below the injection blower as described in Section 5.3.2. The resulting gas flow rates and mean velocities are presented in Table 5.4.2. Gas flow rates calculated by these two methods were within 20%, 29% and 8.3% of one another, for Experiments 1.1, 1.2 and 1.3, respectively. Due to difficulties with the SF₆ gas collection line at the time of experimentation, only hot-wire anemometer results were available for Experiment 2.1. These difficulties stemmed from the fact that the SF₆ had swung out of the experimental reach and into the manhole chamber #2 (See Figure 5.3.2). The darkness and depth of the reach meant that this problem was not identified until after SF₆ gas

collection had taken place. However, a small pointer fixed to the top of the collection line could remedy this problem in future studies.

Table 5.4.2 - Sewer Gas Flow Rates

Experiment	Gas Flow Rate Based on SF ₆ [m ³ /min]	Gas Mean Vel. Based on SF ₆ [m/s]	Gas Flow Rate Based on Anemometer [m ³ /min]	Gas Mean Vel. Based on Anemometer [m/s]
1.1	2.5	0.044	2.0	0.036
1.2	2.1	0.035	1.5	0.024
1.3	11	0.18	12	0.20
2.1	N/A	N/A	1.8	0.15

The gas flow rates listed in Table 5.4.2, may be translated into ventilations rates expressed as number of turnovers of air per day (TuPD). By convention, these turnovers are based on empty pipe volume. Ventilation rates for Experiments 1.1 through 2.1 varied from 22 to 190 TuPD. These ventilation rates are one to two orders of magnitude higher than estimates of natural ventilation rates. Pescod and Price (1981) reported that ventilation rates, required to maintain the 85% of normal oxygen levels typical in atmospheres of many operating sewers, ranged from 0.51 to 2.34 TuPD for 1.50 m and 0.45 m diameter pipes, respectively. Although elevated ventilation rates will have an effect on the gas-phase mass transfer coefficient of a system, they should have a negligible effect on liquid-phase mass transfer coefficients. This is because the ventilation rates were not forceful enough to cause changes in the liquid surface, such as additional surface waves.

5.4.3 VOC Tracer Results

Results of analysis of the gas and liquid samples from Experiments 1.1 through 2.1 are provided in Tables 5.4.3 (a) through 5.4.3 (d). These tables also include information regarding experimental conditions such as wastewater flow rate, wastewater temperature, sewer gas flow rate and sewer gas temperature. Average gas and liquid concentrations were ultimately used to back-calculate mass transfer coefficients as described previously in Section 5.3.1. In the case of gas samples, a time-weighted average (TWA) was used to reflect different lengths of time over which gas samples were collected. Coefficients of variation (Standard Deviation/Arithmetic Mean x 100%) have been included with each set of results to provide an indication of variance amongst the samples. Overall, liquid samples exhibited lower variances than gas samples. Coefficients of variation for liquid samples ranged from 1.7% to 24%, while coefficients of variation for gas samples ranged from 8.9% to 43%.

In addition to analysis of gas and liquid samples, analysis of supplementary checks, such as field blanks and wastewater blanks were included to ensure adequacy of the VOC analyses. The results of these supplementary checks are summarized in Table 5.4.4. Field blanks and breakthrough tubes were observed to have levels of CDCl_3 and TCA that were below the lowest calibration level (BCL) for all of the experiments.

Analysis of wastewater blanks for Experiments 1.2 through 2.1 showed negligible background levels of CDCl_3 and TCA. In Experiments 1.2 and 2.1 background levels were below the lowest calibration level. In Experiment 1.3, levels of CDCl_3 and TCA in the wastewater blank represented 7% and 4% of the levels present in steady state liquid samples. It is believed that, in this situation, inadequate flushing of the peristaltic pump

Table 5.4.3(a) - Results of Experiment 1.1

Experiment 1.1						
Wastewater				Sewer Gas		
Date	Time From/To	Flow Rate [m3/s]	Temperature [C]	pH	DO [mg/L]	TSS [mg/L]
27/05/92	9:25-13:10	0.17	15.6	7.8 - 8.3	1.0 - 1.6	139-164
Temperature [C] 21.6						
Flow Rate [m3/s] 0.042						
Deuterated Chloroform						
Liquid Concentration [ug/L]				Steady State Gas Concentration [ug/L]		
Sample #1				Sample #1		
				Sample #2		
				Sample #3*		
				Sample #4*		
				Sample #5		
				Time Weighted Average:		
				0.38		
				cv = 21%		
1,1,1-Trichloroethane						
Liquid Concentration [ug/L]				Steady State Gas Concentration [ug/L]		
Sample #1				Sample #1		
				Sample #2		
				Sample #3*		
				Sample #4*		
				Sample #5		
				Time Weighted Average:		
				0.20		
				cv = 11%		

* Duplicate gas samples, cv = coefficient of variation

Table 5.4.3(b) - Results of Experiment 1.2

Experiment 1.2									
Date	Time From/To	Wastewater		Temperature [C]	pH	DO [mg/L]	Sewer Gas		
		Flow Rate [m3/s]					Flow Rate [m3/s]	Temperature [C]	
9/6/92	13:33 - 17:05	0.071	16.2	9.0 - 9.3	2.7	139 - 199	0.034	18.0	
Deuterated Chloroform									
Liquid Concentration [ug/L]				Steady State Gas Concentration [ug/L]					
Sample #1				9.2	Sample #1				0.16
Sample #2				14	Sample #2				0.24
Sample #3				17	Sample #3*				0.33
Sample #4				14	Sample #4*				0.41
Average:				13	Time Weighted Average:				0.25
					cv = 24%				cv = 38%
1,1,1-Trichloroethane									
Liquid Concentration [ug/L]				Steady State Gas Concentration [ug/L]					
Sample #1				4.3	Sample #1				0.046
Sample #2				5.3	Sample #2				0.054
Sample #3				4.9	Sample #3*				0.072
Sample #4				5.5	Sample #4*				0.10
Sample #5					Sample #5				0.056
Average:				5.0	Time Weighted Average:				0.06
					cv = 11%				cv = 34%

* Duplicate gas samples, cv = Coefficient of Variation

Table 5.4.3(c) - Results of Experiment 1.3

Experiment 1.3									
Wastewater					Sewer Gas				
Date	Time From/To	Flow Rate [m3/s]	Temperature [C]	pH	DO [mg/L]	TSS [mg/L]	Flow Rate [m3/s]	Temperature [C]	
2/7/92	14:23 - 17:05	0.10	17.0	8.6	0.23	144 - 293	0.18	17.7	
Deuterated Chloroform									
Liquid Concentration [ug/L]					Steady State Gas Concentration [ug/L]				
Sample #1		44			Sample #1				
Sample #2		55			Sample #2				
					Sample #3				
					Sample #4				
Average:		49			cv = 16%		Time Weighted Average:		0.15
									cv = 5.5%
1,1,1-Trichloroethane									
Liquid Concentration [ug/L]					Steady State Gas Concentration [ug/L]				
Sample #1		37			Sample #1				
Sample #2		47			Sample #2				
					Sample #3				
					Sample #4				
Average:		42			cv = 17%		Time Weighted Average:		0.23
									cv = 8.9%

cv = Coefficient of Variation

Table 5.4.3(d) - Results of Experiment 2.1
Experiment 2.1

Experiment 2.1									
Wastewater					Sewer Gas				
Date	Time	Flow Rate	Temperature	pH	DO	TSS	Flow Rate	Temperature	
	From/To	[m3/s]	[C]		[mg/L]	[mg/L]	[m3/s]	[C]	
21/7/92	11:00 - 14:30	0.020	18.9	8.4	4.7	98 - 117	0.030	23.2	
Deuterated Chloroform									
Liquid Concentration [ug/L]					Steady State Gas Concentration [ug/L]				
Sample #1					Sample #1*				
Sample #2					Sample #2*				
Average:					Time Weighted Average:				
94					cv = 2.2%				
93					2.3				
96					cv = 43%				
1,1,1-Trichloroethane									
Liquid Concentration [ug/L]					Steady State Gas Concentration [ug/L]				
Sample #1					Sample #1*				
Sample #2					Sample #2*				
98					2.2				
100					3.4				
Average:					Time Weighted Average:				
99					cv = 1.7%				
2.8					cv = 30%				

* Duplicate gas samples, cv = Coefficient of Variation

head allowed residual amounts of CDCl_3 and TCA from the previous experiment to contaminate the wastewater blank.

Trip spikes were prepared by purging the volatile tracers from a methanol solution. In several cases, the methanol flooded the mass selective detector causing the analysis to abort. The one successful analysis (Experiment 1.2) gave recoveries of 64% and 78% for CDCl_3 and TCA, respectively. but this single sample is not conclusive.

Table 5.4.4. - Supplementary Checks of Experimental VOC Analyses

Supplementary Checks	Chloroform-d (Lowest Calib. Level = 40 ng)	1,1,1 - Trichloroethane (Lowest Calib. Level = 40 ng)
Experiment 1.1		
Field Blank	BCL	BCL
Breakthrough	BCL	BCL
Trip Spike	N/A	N/A
Wastewater Blank	N/A	N/A
Experiment 1.2		
Field Blank	BCL	BCL
Breakthrough	BCL	BCL
Trip Spike	64%	78%
Wastewater Blank	BCL	BCL
Experiment 1.3		
Field Blank	BCL	BCL
Breakthrough	BCL	BCL
Trip Spike	N/A	N/A
Wastewater Blank	7%	4%

Table 5.4.4. - Continued

Supplementary Checks	Chloroform-d (Lowest Calib. Level = 40 ng)	1,1,1 - Trichloroethane (Lowest Calib. Level = 40 ng)
Experiment 2.1		
Field Blank	BCL	BCL
Breakthrough	BCL	BCL
Trip Spike	N/A	N/A
Wastewater Blank	BCL	BCL

BCL - Below Lowest Calibration Level

In examining VOC tracer results, it was valuable to perform mass balances on each of the experiments. This balance was made by comparing tracer mass flows into the system with tracer mass flows out of the system. Mass flow into the reach was taken to be the gravimetric concentration of CDCl_3 or TCA in the Tedlar® bag used for injection, multiplied by the tracer injection rate. Mass flow out of the system was taken to be the average measured liquid concentration of the tracer, multiplied by the wastewater flow rate, plus the TWA gas concentration of the tracer, multiplied by the sewer gas flow rate. A summary of these mass balances is provided in Table 5.4.5. Included in the table is an additional column indicating what the predicted liquid concentration would be based on the gravimetric Tedlar® bag concentration.

Table 5.4.5 - Mass Balances

	Gravimetric Tedlar Bag Concentration [mg/L]	VOC Tracer Injection Rate [mL/min]	Measured Liquid Conc. [ug/L]	Wastewater Flow Rate [m3/s]	Gas Conc. [ug/L]	Sewer Gas Flow Rate [m3/sec]	Predicted Liquid Conc. Based on Gravimetric		Mass Closure [%]
								[ug/L]	
Experiment 1.1									
Chloroform-d	625	181	18	0.17	0.38	0.042	11		162
1,1,1-Trichloroethane	558	181	8.4	0.17	0.20	0.042	10		84
Experiment 1.2									
Chloroform-d	625	107	13	0.071	0.25	0.034	16		87
1,1,1-Trichloroethane	558	107	5.0	0.071	0.061	0.034	14		36
Experiment 1.3									
Chloroform-d	625	383	49	0.10	0.15	0.18	41		122
1,1,1-Trichloroethane	558	383	42	0.10	0.23	0.18	36		118
Experiment 2.1									
Chloroform-d	312	160	94	0.020	2.3	0.030	41		240
1,1,1-Trichloroethane	279	160	99	0.020	2.8	0.030	37		281

The degree of mass closure for chloroform-d in Experiment 1.1 (162%) and 1,1,1-trichloroethane in Experiment 1.2 (36%) are poor. However, average mass closure for the first three experiments is 101%, meaning that the results surround unity. Mass closures for Experiment 2.1 are also poor. This is essentially due to the discrepancy between the measured liquid concentration and the predicted liquid concentration based on the gravimetric Tedlar bag concentration. Measured and predicted concentrations differed by a factor of 2.3 for chloroform-d and by a factor of 2.7 for 1,1,1-trichloroethane. These discrepancies could be caused by poor mixing of the tracers in the liquid-phase of the sewer reach. It is possible that with such swift flow along a short reach, channeling of the tracers occurred. This explanation seems plausible given that the tracers had equally elevated measured liquid concentrations. However, these discrepancies could also have resulted from some combination of experimental inaccuracies, including inaccuracies in tracer solution preparation, tracer solution injection rate and compound calibration curves.

5.4.4 Overall Mass Transfer Coefficients

Table 5.4.6 summarizes the sewer reach operating characteristics and compares them to the experimental reaches studied by Corsi (1989) and Jensen and Hvitved-Jacobsen (1990). Although the reaches have been placed in order of increasing pipe diameter, it is interesting to note that Guelph #1 fits between the Davis and Sacramento reaches. Its pipe diameter, slope, wastewater flow rates, and even gas flow rates fill the gap between the two California reaches. Guelph #2, however, is a much more extreme reach, a small 0.52 m pipe laid on a 3.5% grade with a shallow, swift wastewater flow of 0.02 m³/s. The most notable feature of the Aalborg reach in Denmark was the 2.3 km length over which the experiments were conducted.

Table 5.4.6 - Operating Characteristics of Experimental Sewer Reaches

Characteristic	Davis	Guelph #2	Aalborg	Guelph #1	Sacramento
Diameter [m]	0.5	0.52	0.6 - 0.7	1.2	2.6
Slope [%]	0.2	4	0.09	0.1	0.06
W W Flow [m ³ /s]	0.03-0.06	0.02	0.018-0.021	0.07-0.17	2.1-2.6
Gas Flow [m ³ /s]	0.02-0.03	0.03	@	0.04	1.8
Length [m]	131	64	2310	122	291

@ Aalborg experimental reach was not force ventilated and natural ventilation rates were not reported.

Experimental mass transfer coefficients were back-calculated using the CORAL model. Experimental conditions were specified, and the measured liquid concentration at the downstream manhole was taken to be the upstream VOC discharge concentration. Through an iterative process, different overall mass transfer coefficients were provided to the model until the steady-state gas concentration calculated by the model matched the measured (TWA) gas concentration. Assuming that the upstream and downstream liquid concentrations were identical does not introduce significant error into the backcalculation process. In many mass transfer experiments, changes in liquid concentration are employed to indirectly calculate gas-liquid mass transfer coefficients. All mass lost from the liquid-phase is assumed to have been transferred to the gas-phase of the system. However, the change in liquid concentration over the relatively short distances involved in this set of experiments was insignificant, making upstream and downstream concentrations indistinguishable, and making steady-state gas samples essential in evaluating gas-liquid mass transfer coefficients.

After experimental mass transfer coefficients had been determined, the CORAL model was used to predict overall mass transfer coefficients. The CORAL predictions were based on Equation 8. Modelled mass transfer coefficients were then converted from oxygen to CDCl_3 and TCA, using ψ ratios of 0.57 and 0.50, respectively. Table 5.4.7 provides a comparison of experimental and predicted mass transfer coefficients. Mass transfer coefficients have also been normalized by mean hydraulic depth, yielding units of hr^{-1} . These normalized values have been included in Table 5.4.7 to provide consistency between current comparisons and those completed by Corsi (1989) and Jensen and Hvitved-Jacobsen (1990). Mass transfer coefficients predicted by these authors are also based upon diffusion adjustments to the Parkhurst and Pomeroy model (Equation 8).

Table 5.4.7 - Experimental and Predicted Mass Transfer Coefficients

Site	Compound	K exp. [m/hr]	K pred. [m/hr]	K exp. [hr ⁻¹]	K pred. [hr ⁻¹]
<u>GUELPH #1</u>					
Experiment 1.1	Chloroform-d	0.028	0.034	0.13	0.16
	1,1,1-Trichloroethane	0.029	0.030	0.13	0.14
Experiment 1.2	Chloroform-d	0.025	0.032	0.18	0.23
	1,1,1-Trichloroethane	0.015	0.027	0.11	0.20
Experiment 1.3	Chloroform-d	0.017	0.033	0.10	0.20
	1,1,1-Trichloroethane	0.030	0.029	0.18	0.18
<u>GUELPH #2</u>					
Experiment 2.1	Chloroform-d	0.15 [†]	0.35	3.6 [†]	8.5
		0.45 [‡]		11 [‡]	
	1,1,1-Trichloroethane	0.15 [†]	0.30	3.7 [†]	7.3
		0.44 [‡]		11 [‡]	

Table 5.4.7 - Continued

Site	Compound	K exp. [m/hr]	K pred. [m/hr]	K exp. [hr ⁻¹]	K pred. [hr ⁻¹]
<u>AALBORG</u>					
05.10.88	Oxygen			0.50	0.43
26.10.88 (a)	Oxygen			0.52	0.43
26.10.88 (b)	Oxygen			0.52	0.43
<u>DAVIS</u>					
Test #1	Chloroform-d			0.28	0.41
Test #2	Chloroform-d			0.51	0.41
Test #3	Chloroform-d			0.48	0.48
Test #4	Chloroform-d			0.76	0.51
<u>SACRAMENTO</u>					
Test #5	Chloroform-d			0.032	0.059
Test #6	Chloroform-d			0.056	0.059

† Experimental mass transfer coefficient calculated based on liquid sample measurements.

‡ Experimental mass transfer coefficient calculated based on predicted liquid concentration.

Predicted mass transfer coefficients agreed with experimental mass transfer coefficients to within a factor of 2. This was also true of the results published by Corsi and Jensen and Hvitved-Jacobsen. In addition, as the operating characteristics of Guelph #1 fell in between those of the Davis and Sacramento reaches, one would expect the mass transfer coefficients for Guelph #1 to fall between those reported for Davis and Sacramento. This was the case. The average mass transfer coefficients for the Davis, Guelph #1, and Sacramento reaches were 0.51, 0.14 and 0.044 hr⁻¹, respectively.

Finally, in moving the experiments from Guelph #1 to Guelph #2, the model predicted an order of magnitude increase in mass transfer coefficients, and the experimental results, in fact, confirm an order of magnitude increase in mass transfer coefficients for both volatile tracers. As it was difficult to ascertain whether the liquid concentration measured in Experiment 2.1 was more reliable than the predicted liquid concentration based on the gravimetric injection concentration, both were used to make separate determinations of experimental mass transfer coefficients. For both CDCl_3 and TCA, resulting ranges of mass transfer coefficients encompassed the predicted mass transfer coefficient. Experimental values of 3.6 and 11 hr^{-1} surround the predicted value of 8.5 hr^{-1} for CDCl_3 and experimental values of 3.7 and 11 hr^{-1} surround the predicted value of 7.3 hr^{-1} for TCA.

Evidence supports the use of Parkhurst and Pomeroy's model and published adjustment (ψ) ratios in predicting gas-liquid mass transfer coefficients for VOCs along uniform sewer reaches with a wide range of system operating conditions. As this approach is embedded within the CORAL fate/transport model, this evidence also reinforces the gas-liquid mass transfer simulations produced by this existing computational model.

5.4.5 Uncertainties

The following analysis was undertaken to place bounds on the experimental mass transfer coefficients obtained in this study. An estimate of potential error, or overall uncertainty, was made using the error propagation technique. Within the four field experiments completed in Guelph, the change in concentration driving force, along the

uniform sewer reach was negligible. Therefore, Equation 1 may be used to approximate the mass transfer coefficient. Equation 1 was rearranged as follows:

$$-K = \frac{R}{\left(C_l - \frac{C_g}{H_c}\right)A} \quad (13)$$

The rate of mass transfer, R, was equated to the product of the ventilation rate and the gas-phase concentration, $Q_v C_g$, resulting in Equation 14.

$$-K = \frac{Q_v C_g}{\left(C_l - \frac{C_g}{H_c}\right)A} \quad (14)$$

By differentiating Equation 14, with respect to all other variables in the equation, an estimate of the error associated with the mass transfer coefficient, K, was developed. Substituting in specific values of ventilation rate, Q_v , gas-phase concentration, C_g , liquid-phase concentration, C_l , Henry's law constant, H_c , and interfacial area, A, in addition to the uncertainties associated with each of these parameters resulted in different overall uncertainties for each experiment and tracer compound.

Estimates of the individual uncertainties associated with ventilation rate, gas-phase concentration, liquid-phase concentration, Henry's law constant, and interfacial area are summarized in Table 5.4.8. Conservative uncertainties were assumed. For example:

1. Ventilation Rate Q_V : Sulfur hexafluoride samples used in determining ventilation rates were assumed to be collected at steady-state. Therefore the largest coefficient of variation of measured SF_6 values, $\pm 17\%$, was used as an worst-case estimate of the uncertainty associated with ventilation rate. Uncertainty in ventilation rate stemmed from factors such as uncertainties in sulfur hexafluoride injection rates, calibration standards and the manual injection of sub-samples during analysis.
2. Gas- and Liquid-phase Concentrations C_g, C_l : Gas-phase and liquid-phase samples collected during each experiment were assumed to be at steady-state. Therefore, uncertainties associated with gas-phase and liquid phase concentrations were taken to be the largest coefficients of variation which occurred over these steady-state samples. This approach resulted in an individual uncertainties of $\pm 43\%$ and $\pm 24\%$, for gas-phase and liquid-phase concentrations, respectively. These uncertainties are assumed to encompass all sources of error surrounding VOC sampling and analysis including: liquid and gas sample losses, variances in VOC tracer injection, variances in gas sampling flow rates, errors in gas sample timing, and uncertainties in calibration standards.
3. Henry's Law Constant, H_C : Uncertainty surrounding the Henry's law constants for both tracer compounds was estimated to be $\pm 15\%$, based on differences in published values (Gossett, 1987; Ashworth, 1988). Differences between clean water and wastewater H_C were not accounted for due to a lack of published literature.
4. Interfacial Area, A : Uncertainty in interfacial area was based on the potential error in the calculation of wastewater flow rates. Average quenching of rhodamine dye samples which were used in determining wastewater flow rates was observed to be 9%. However, the mass deficit presented in Figure 5.4.1, indicated that losses of

rhodamine dye, and hence, errors in wastewater flow rates may have ranged from 10% to 20%. Therefore, a worst-case uncertainty of the $\pm 20\%$ was assigned to interfacial area. Uncertainty in wastewater flow rate and thus interfacial area were assumed to stem from individual uncertainties involving the preparation of rhodamine injection solutions, rhodamine dye injection rates, and quenching effects and variations in calibration standards.

Table 5.4.8 - Individual Uncertainties

Variable	Uncertainty
Ventilation Rate, Q_v	$\pm 17\%$
Gas-phase concentration, C_g	$\pm 43\%$
Liquid-phase concentration, C_l	$\pm 24\%$
Henry's law constant, H_c	$\pm 15\%$
Interfacial area, A	$\pm 20\%$

These individual uncertainties may be combined to approximate the overall uncertainty or potential error in experimentally determined mass transfer coefficients. A summary of these overall uncertainties is presented in Table 5.4.9. For all experiments, the largest individual uncertainties were those associated with gas and liquid-phase tracer concentrations. The overall uncertainty in K associated with each experiment was approximately a factor of 2 (100%). Details regarding differentiation and specific calculations are provided in Appendix B.

Table 5.4.9 - Overall Uncertainty Associated with Experimental Mass Transfer Coefficients

	Chloroform-d		1,1,1-Trichloroethane	
	K (hr ⁻¹)	Overall Uncertainty [%]	K (hr ⁻¹)	Overall Uncertainty [%]
Experiment 1.1	0.13	120	0.13	110
Experiment 1.2	0.18	130	0.11	100
Experiment 1.3	0.10	110	0.18	110
Experiment 2.1	3.6	110	3.7	100

Gas-liquid mass transfer of volatile organic compounds along uniform sewer reaches was investigated both computationally and experimentally. Computational modelling was used to estimate VOC emissions under a wide range of conditions, while field experimentation led to the determination of mass transfer coefficients and the subsequent evaluation of a semi-empirical model used to predict gas-liquid mass transfer coefficients.

The results of model simulations has led to several conclusions. *Overall mass removal of VOCs along uniform sewer reaches is insensitive to system hydrodynamics.* Even along a 1 km reach, the maximum difference in fractional mass removal which resulted from treating the system as a single well-mixed reactor, as opposed to a plug-flow system, was 7%. This means that *relatively long portions of sewer networks may be treated as single reactors, without incurring large errors in estimated VOC emissions.* This is particularly true considering the high uncertainties in other parameters (e.g., magnitude of ventilation), required for emissions estimates.

Overall mass removal is also relatively insensitive to spatial patterns of ventilation. Over the majority of scenarios tested within this study, variation in ventilation pattern caused no more than a 13% change in overall mass removal. However, changes in fractional mass removal were more pronounced under higher ventilation conditions. For one of the model runs, an order of magnitude increase in ventilation rate meant that variation in ventilation pattern was capable of producing a 22% change in overall mass removal.

Overall mass removal from uniform sewer reaches is highly sensitive to the magnitude of ventilation. Increasing the ventilation rate from 1 volume turnover per day to 10 turnovers per day produced an average 520% increase in overall mass removal for the three compounds tested (chloroform, trichloroethylene and carbon tetrachloride). The lowest volatility compound, chloroform, exhibited the highest average increase, 700%. Therefore, proper quantification of head space ventilation rates is fundamental to developing accurate VOC emissions estimates.

In general, relative removal of VOCs along 1 to 2 km sewer reaches is low (< 10%). In those instances in which higher relative mass removals were predicted, it was not possible to identify the exact contribution of each factor. However, the following conditions generally led to relatively high losses from sewer reaches: low relative depths, high channel slope, high ventilation rates and high Henry's law constants.

Diffusivity-adjustment of Parkhurst and Pomeroy's model represents an appropriate method for estimating liquid-phase mass transfer coefficients along uniform sewer reaches. Even under the extreme conditions tested in this research, mass transfer coefficients based on Parkhurst and Pomeroy's model were within a factor of 2 of experimentally determined mass transfer coefficients.

Field experiments completed along two municipal sewer reaches in Guelph exhibited mass transfer coefficients that were in reasonable agreement with published values from mass transfer experiments along sewer reaches in California and Denmark. Reasonable estimates of mass transfer coefficients were obtained using Parkhurst and Pomeroy's semi-empirical model for predicting reaeration in sewer environments combined with theoretical ratios relating oxygen and VOC liquid molecular diffusion coefficients. In the final experiment, which took place along a steep reach (3.5% channel slope), with

mean wastewater velocity of 1.5 m/s, the model predicted an order of magnitude increase in the mass transfer coefficient, and this increase was, in fact, observed.

Finally, although the aforementioned experiments required extensive preparation and analysis, they demonstrated the feasibility of obtaining mass transfer coefficients from controlled field experiments.

Computational modelling should continue to be used as a tool for investigating gas-liquid mass transfer along sewer reaches. The hundreds of model runs completed as part of this research have facilitated sensitivity analyses and the identification of situations which can lead to unusually high VOC emissions. Additional modelling exercises could examine more detailed aspects of this mechanism, such as, the sensitivity of overall mass removal to mass transfer coefficient. The purpose of this analysis would be to identify conditions under which overall mass removal varies little with mass transfer coefficient, i.e., the realm over which very rough approximations of mass transfer coefficient would suffice for VOC emissions estimates. The impact of countercurrent air flow, where gas and liquid streams travel in opposite directions, should be evaluated and the importance of interactions between gas-liquid mass transfer and other fate mechanisms, such as adsorption and biodegradation, should be also be investigated.

The general trends, insensitivities and sensitivities that have been identified with regards to gas-liquid mass transfer and overall mass removal should be included in the design and development of an MOE advanced fate/transport model. The results of both computational modelling and experimentation should permit valid simplifications and approximations to be incorporated into an advanced sewer fate/transport model, which must simulate vast networks in a timely, yet realistic manner.

Additional field experiments should be completed with lower volatility tracer compounds for which gas-phase resistance may play a significant role. Important considerations for such experiments would include ventilation rates and sorption to solids. Gas-phase resistance will be affected by the different degrees of gaseous mixing imposed

by different ventilation rates. In addition, lower volatility compounds often exhibit greater affinity for solids, meaning that sorption to solids may have to be considered within the experimental design or an extensive investigation may be required to find a suitable low volatility tracer exhibiting minimal sorption.

Several related investigations should be undertaken in future field work. First, a more extensive study regarding the magnitude of natural ventilation along sewer reaches is warranted given the results of computational modelling. Second, gas-liquid mass transfer at drop structures, including drop manholes and pump stations, should be examined to provide an estimate of the relative importance of gas-liquid mass transfer at these appurtenances. Third, as computational modelling results also pointed to the impact of low relative depth of flow on overall mass removal, field experiments could verify the importance of low wastewater flow. Fourth, given that only one field experiment was completed along a sewer reach with a steep channel slope, additional experiments along other steep reaches would be valuable in substantiating present results and providing information regarding moderately steep channel slopes (eg., 1% to 3%). Finally, all experiments carried out to date have involved relatively large municipal sewer reaches (pipe diameters > 0.5 m). Similar experiments to those described in this research should be conducted along small industrial sewers (pipe diameters < 0.5 m) such as those which feed wastewater pretreatment processes at industrial facilities and small residential sewer reaches which typically connect households to sanitary/storm sewer systems.

Ashworth, R.A., Howe, G.B., Mullins, M.E., and Rogers, T.N., "Air-Water Partitioning Coefficients of Organics in Dilute Aqueous Solutions", Journal of Hazardous Materials, Vol. 18, 1988, pp.25 - 36.

Bell, J.P., Osinga, I., and Melcer, H., "Investigation of Stripping of Volatile Organic Contaminants in Municipal Wastewater Treatment Systems, Phase I", Queen's Printer for Ontario, December, 1988.

Cadwallader, T.E., and McDonnell, A.J., "A Multivariate Analysis of Reaeration Data", Water Research, Vol. 3, 1969, pp. 731-742.

Corsi, R.L., Chang, D.P.Y., Schroeder, E.D., and Qingzeng, Q., "Emissions of Volatile and Potentially Toxic Organic Compounds from Municipal Wastewater Treatment Plants", Annual Meeting of the Air Pollution Control Association, New York, 1987.

Corsi, R.L., *Volatile Organic Compound Emissions from Wastewater Collection Systems*, Doctoral Dissertation, University of California, Davis, (1989).

Corsi, R.L., "VOC Emissions from Sewers", Proceedings of the Annual Meeting of the Water Environment Federation, Toronto, 1991.

Corsi, R.L., University of Guelph, personal communication, 1992 (a).

Corsi, R.L., Chang, D.P.Y., Schroeder, E.D., " A Modelling Approach for VOC Emissions from Sewers", Water Environment Research, Vol. 64, No. 5, 1992 (b), pp. 734-741.

Corsi, R.L., *et al.*, "Fate of Volatile Organic Compounds in Municipal Wastewater Collection Systems", Poster presented at the Ontario Ministry of the Environment's Technology Transfer Conference, Toronto, November, 1992 (c).

Danckwerts, P.V., "Significance of Liquid Film Coefficients in Gas Absorption", Industrial and Engineering Chemistry, Vol. 43, No. 6, 1951, pp. 1460-1467.

Dobbins, W.E., "Mechanism of Gas Absorption by Turbulent Liquids", in Advances in Water Pollution Research, Vol. 2, W.W. Eckenfelder, ed., Pergamon Press, Ltd., New York, 1964, pp. 61-96.

Gossett, J.M., "Measurement of Henry's Law Constants for C1 and C2 Chlorinated Hydrocarbons", Environmental Science and Technology, Vol. 21, No. 2, 1987, pp. 202-208.

Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Volume II, Howard, P.H. Editor, Lewis Publishers, Inc., Chelsea, Michigan, 1990.

Higbie, R., "The Rate of Exposure of a Pure Gas into a Still Liquid During Short Periods of Exposure", Transactions, American Inst. of Chem. Engrs., Vol. 31, 1935.

Huang, J.Y.C., Wilson, G.E., and Schroepfer, T.W., "Evaluation of Activated Carbon Adsorption for Sewer Odor Control", Journal of the Water Pollution Control Federation, Vol. 51, No. 5, 1979, pp. 1054-1062.

Jensen, N.A., and Hvitved-Jacobsen, T., "Method of Measurement of Reaeration in Gravity Sewers Using Radiotracers", Journal of the Water Pollution Control Federation, Vol. 63, No. 5, 1991, pp. 758-767.

Krenkel, P.A. and Orlob, G.T., "Turbulent Diffusion and the Reaeration Coefficient", Journal of the Sanitary Engineering Division, ASCE, Vol. 88, No. SA2, Proc. Paper 3079, March, 1962, pp. 53-83.

Levins, P., *et al.*, Sources of Toxic Pollutants Found in Influent to Sewage Treatment Plants 6. Integrated Interpretation, EPA/440/4-81/007, U.S. Environmental Protection Agency, Washington, D.C., 1979.

Lewis, W.K., and Whitman, W.G., "Principles of Gas Absorption", Industrial and Engineering Chemistry, Vol. 16, No. 12, 1924, pp. 1215-1220.

Matter-Muller, C., Gujer, W. and Giger, W., "Transfer of Volatile Substances from Water to Atmosphere", Water Research, Vol. 15, 1981, pp. 1271-1279.

Melcer, H., Thompson, D., Bell, J., Monteith, H., "Stripping of Volatile Organic Compounds at Municipal Wastewater Treatment Plants", AWM/EPA International Symposium on Hazardous Waste Treatment: Biosystem for Pollution Control, Cincinnati, 1989.

Munz, C., and Roberts, P.V., "Gas and Liquid-Phase Mass Transfer Resistances of Organic Compounds During Mechanical Surface Aeration", Water Resources, Vol. 23, No. 5, 1989, pp. 589 - 601.

Namkung, E., and Rittmann, B.E., "Estimating Volatile Organic Compound Emissions from Publicly Owned Treatment Works", Journal of the Water Pollution Control Federation, Vol. 59, No. 7, 1984, pp. 518 - 521.

O'Connor, D.J., and Dobbins, W.E., "Mechanisms of Reaeration in Natural Streams", Transactions, ASCE, Vol. 123, Paper No. 2934, 1958, pp. 641-684.

Parkhurst, J.D., and Pomeroy, R.D., "Oxygen Absorption in Streams", Journal of the Sanitary Engineering Division, ASCE, Vol. 98, No. SA1, Proc. Paper 8701, 1972, pp. 101-124.

Pescod, M.B., and Price, A.C., "Fundamentals of Sewer Ventilation as Applied to the Tyneside Sewerage Scheme", Water Pollution Control, 1981, pp. 17-33.

Pincince, A.B., "Transfer of Oxygen and Emissions of Volatile Organic Compounds at Clarifier Wiers", Proceedings of the WPCF/EPA Workshop on Air Toxics Emissions and POTWs, Alexandria, Virginia, 1989.

Reid, J.M., and McEvoy, M., "Monitoring Sewer Atmospheres for Organic Vapour", Journal of the Inst. of Water & Env. Mgmt. Vol. 1, No. 2, 1987, pp. 161-170.

Seinfeld, J., Atmospheric Chemistry and Physics of Air Pollution, John Wiley and Sons Inc., New York, 1986, pp 60-65.

Smith, J.H., Bomberger, D.C., and Haynes, D.L., "Prediction of the Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies", Environmental Science and Technology, Vol. 14, No. 11, 1980, pp. 1332-1337.

Streeter, H.W., Wright, C.T., and Kehr, R.W., "Measures of Natural Oxidation in Polluted Streams. III. An Experimental Study of Atmospheric Reaeration Under Stream-Flow Conditions," Sewage Works Journal, Vol. 8, No. 2, March, 1936, pp. 282-316.

Standard Methods for the Examination of Water and Wastewater, 17th Ed., American Public Health Association, Washington D.C., 1989.

Tsivoglou, E.C., *et al.*, "Tracer Measurements of Reaeration: I. Laboratory Studies", Journal of the Water Pollution Control Federation, Vol 37, 1965, pp.1343-1362 .

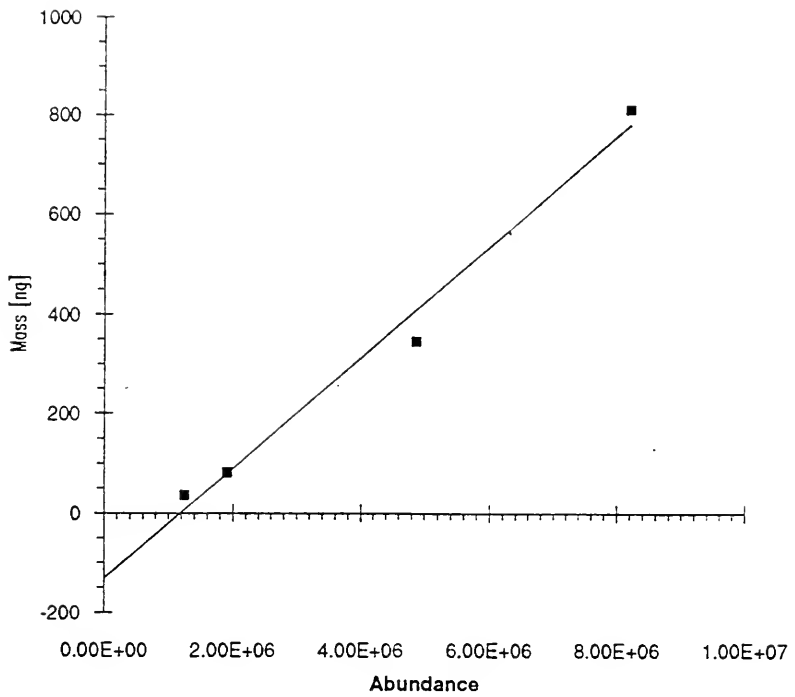
Tsivoglou, E.C., and Neal, L.A., "Tracer Measurements of Reaeration: II. Predicting the Reaeration Capacity of Inland Streams", Journal of the Water Pollution Control Federation, Vol 48, No. 12, 1976, pp.2669 .

United States Environmental Protection Agency (1986), Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works, EPA/530-SW-86-004, U.S. Environmental Protection Agency, Washington, D.C..

Whitmore, A., Corsi, R.L., Thompson, D., and Shepherd, J., "Examining Volatile and Semi-Volatile Organic Compounds Along Uniform Sewer Reaches", Proceedings of the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, 1992.

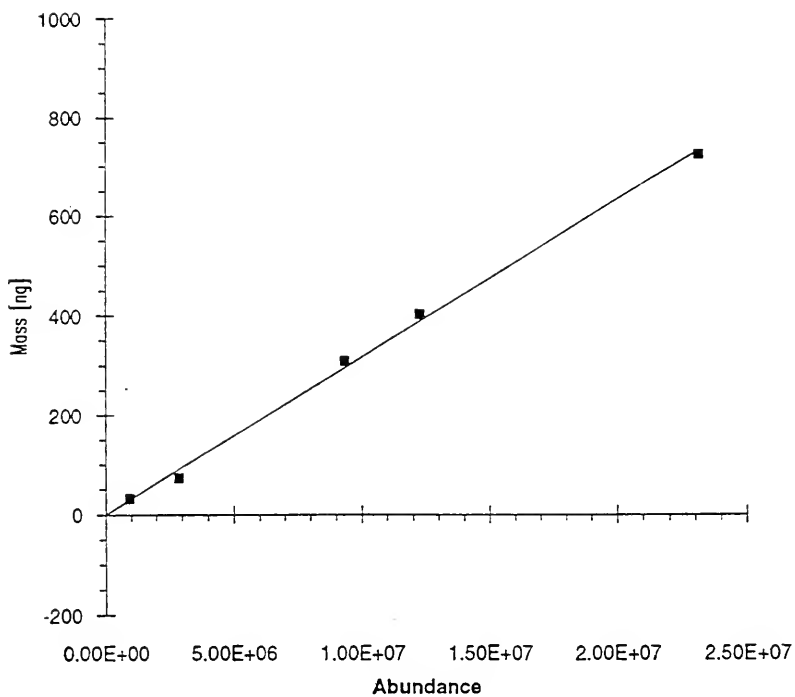
APPENDIX A : CALIBRATION CURVES

Experiment 1.1 - Chloroform-d



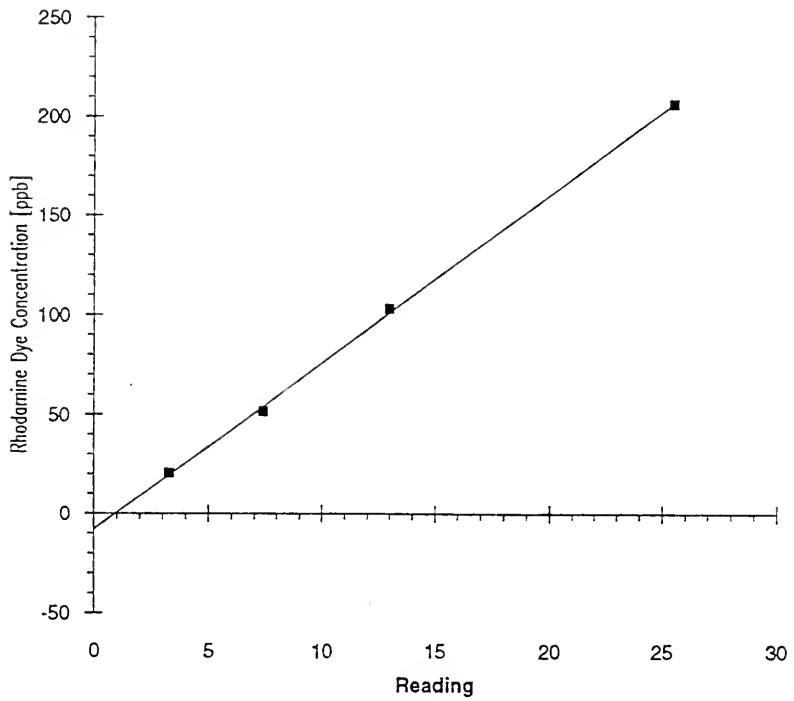
$$R^2 = 0.98$$

Experiment 1.1 - 1,1,1-Trichloroethane



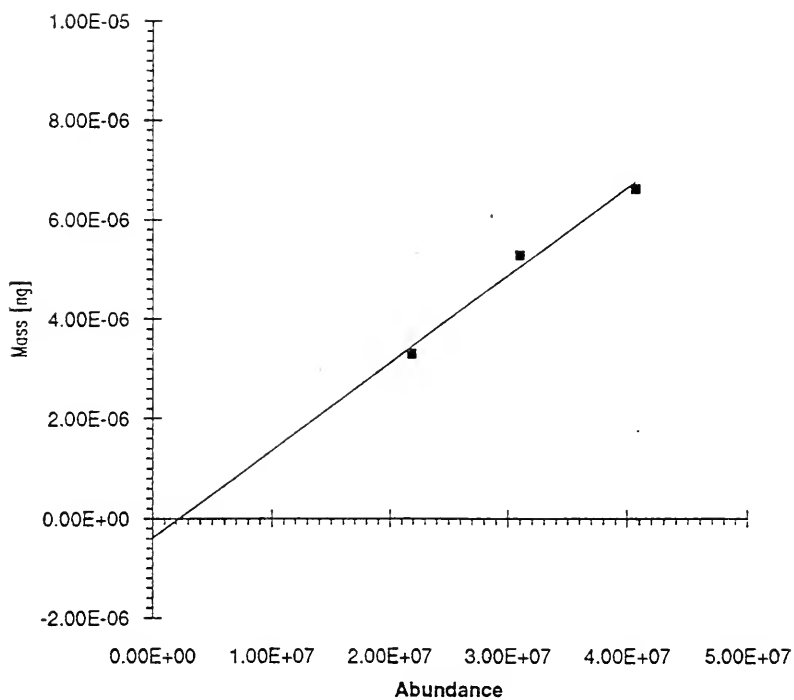
$R^2 = 0.99$

Experiment 1.1 - Rhodamine Dye



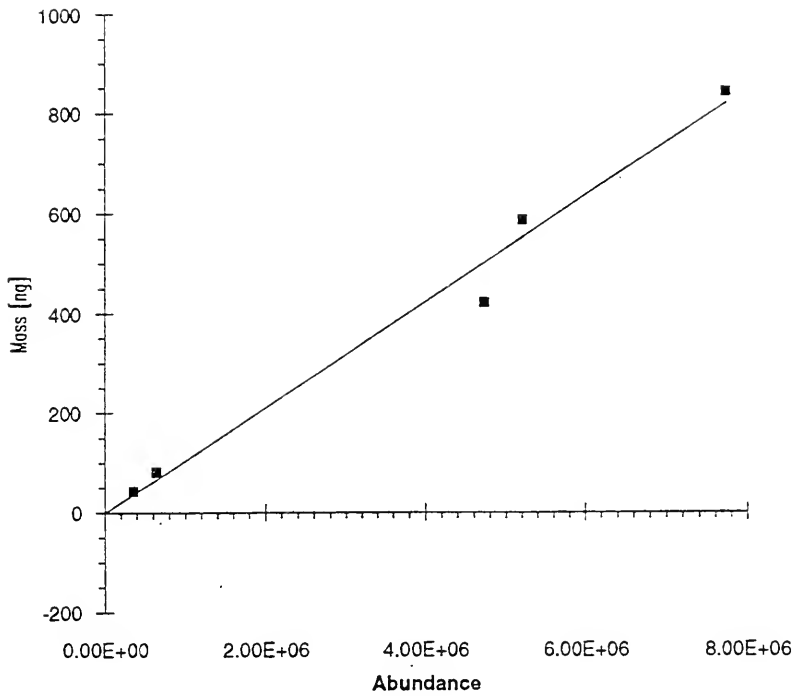
$$R^2 = 0.99$$

Experiment 1.1 - Sulfur Hexafluoride



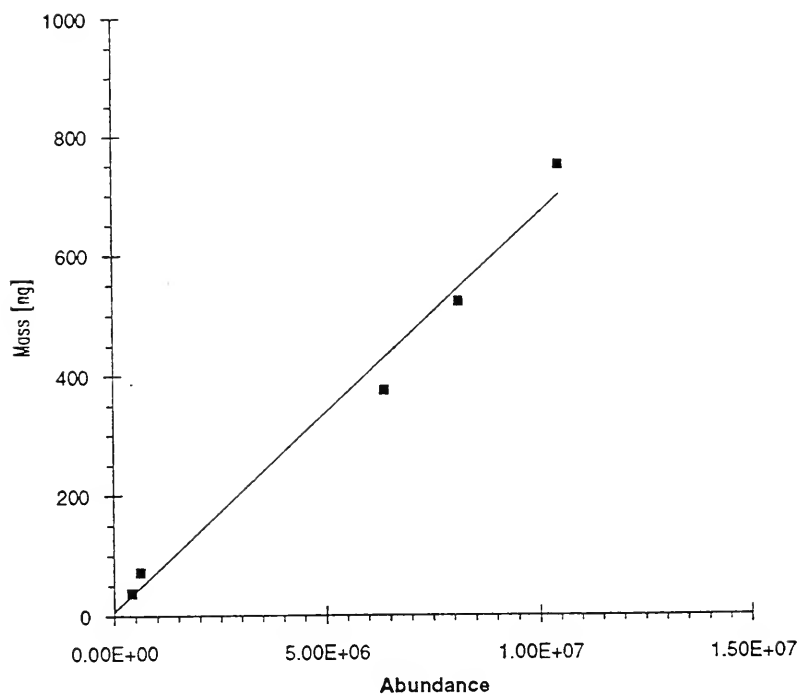
$$R^2 = 0.98$$

Experiment 1.2 - Chloroform-d



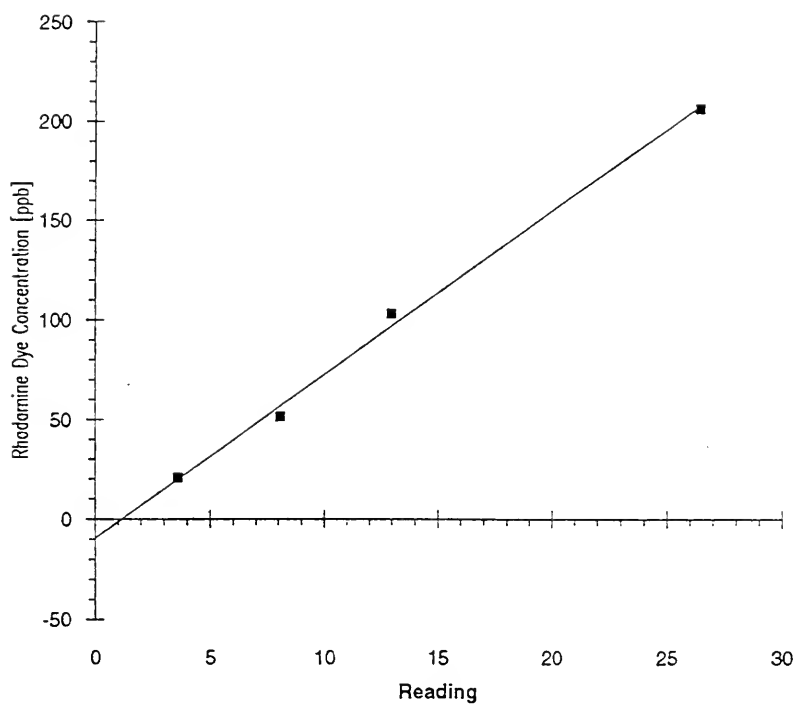
$R^2 = 0.98$

Experiment 1.2 - 1,1,1-Trichloroethane



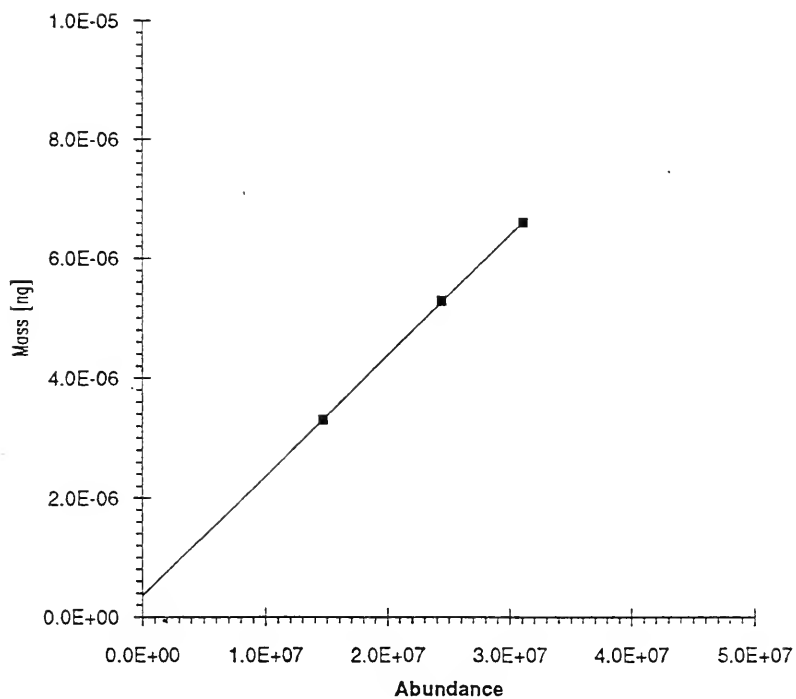
$$R^2 = 0.98$$

Experiment 1.2 - Rhodamine Dye



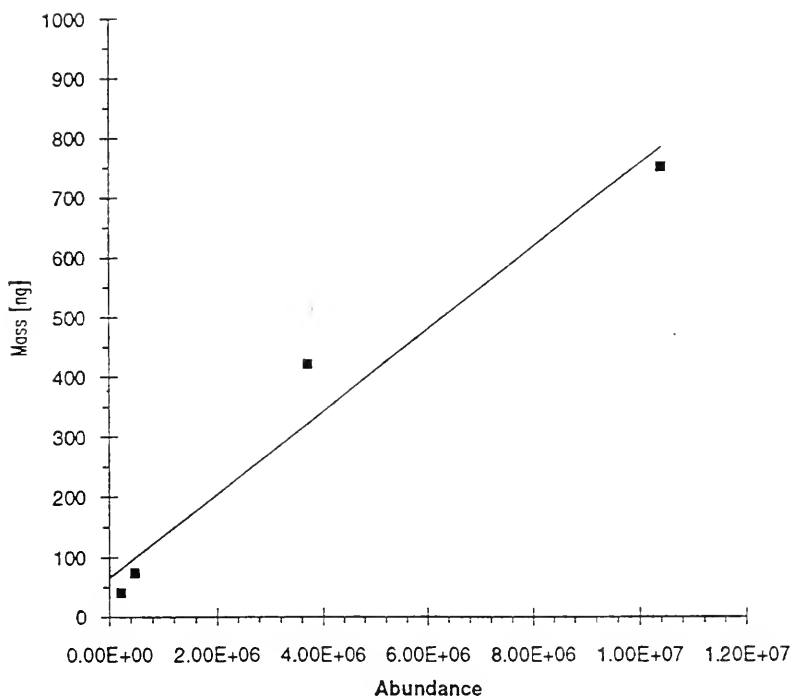
$$R^2 = 0.99$$

Experiment 1.2 - Sulfur Hexafluoride



$$R^2 = 0.99$$

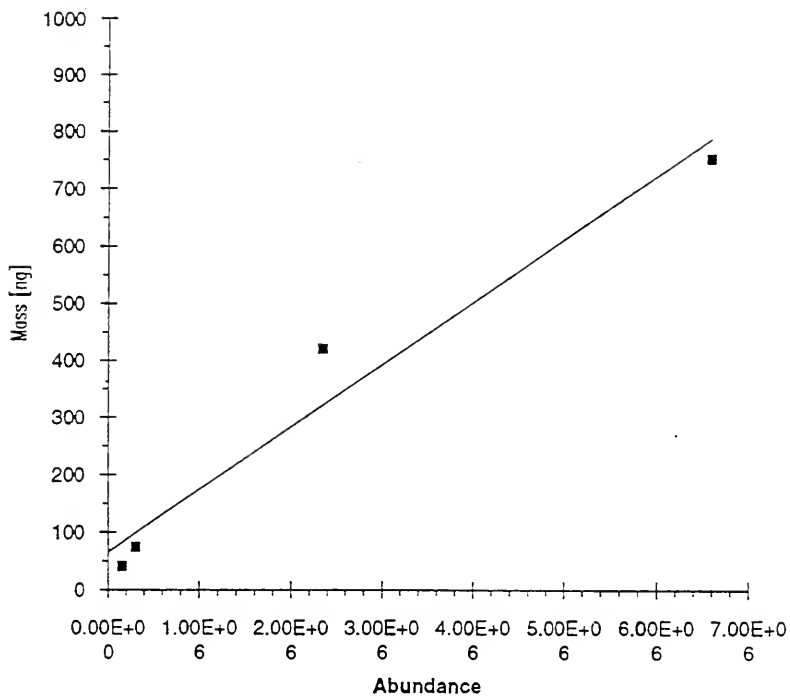
Experiment 1.3 - Chloroform-d *



$$R^2 = 0.96$$

* Based on Ion 84 - used to quantify mass in liquid samples

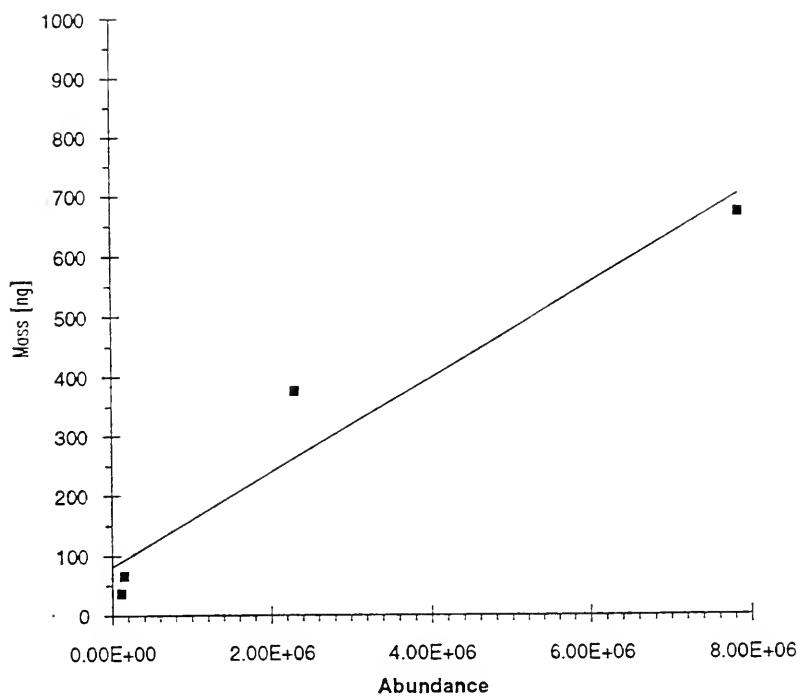
Experiment 1.3 - Chloroform-d **



$$R^2 = 0.96$$

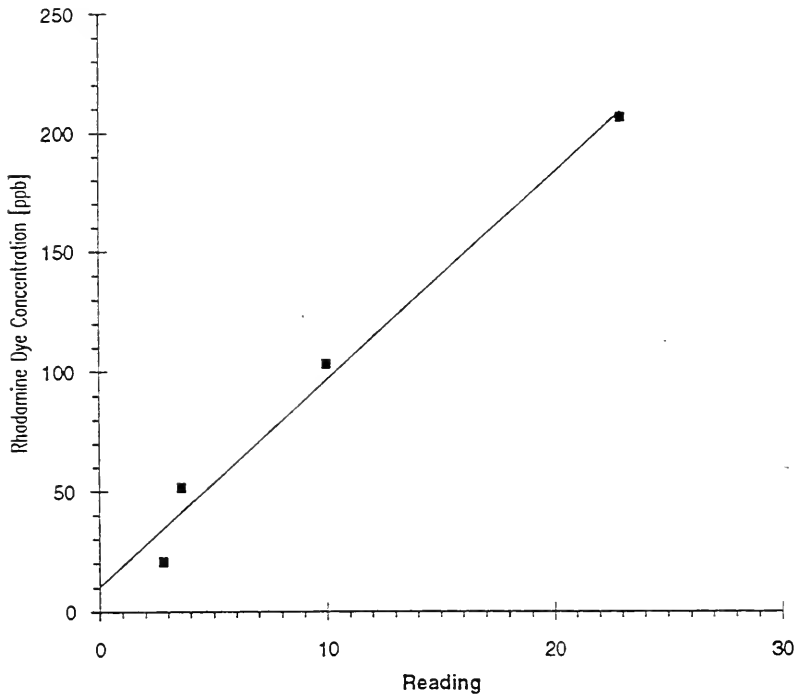
** Based on Ion 86 - used as an alternate ion to quantify mass on gas samples, because of interference between chloroform-d and dichloromethane

Experiment 1.3 - 1,1,1-Trichloroethane



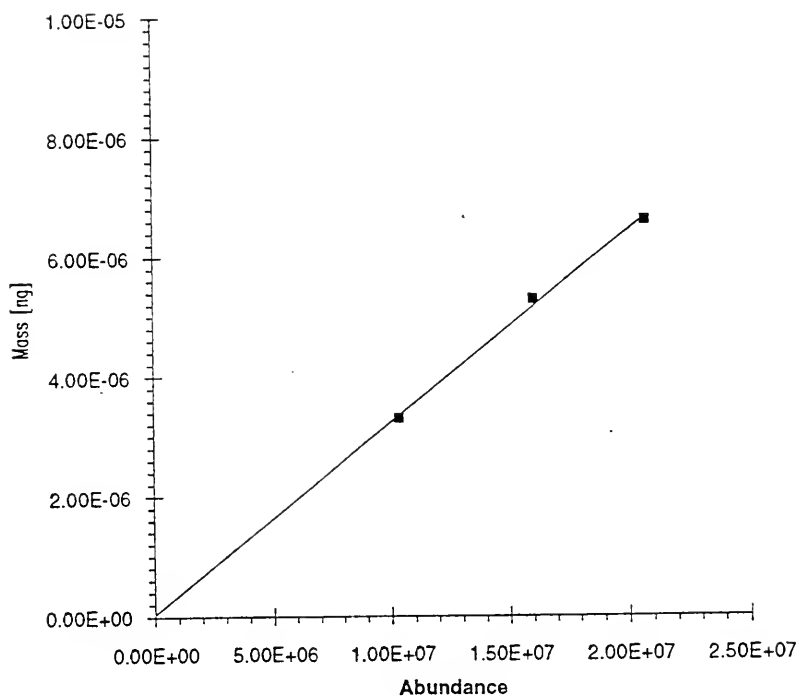
$$R^2 = 0.94$$

Experiment 1.3 - Rhodamine Dye



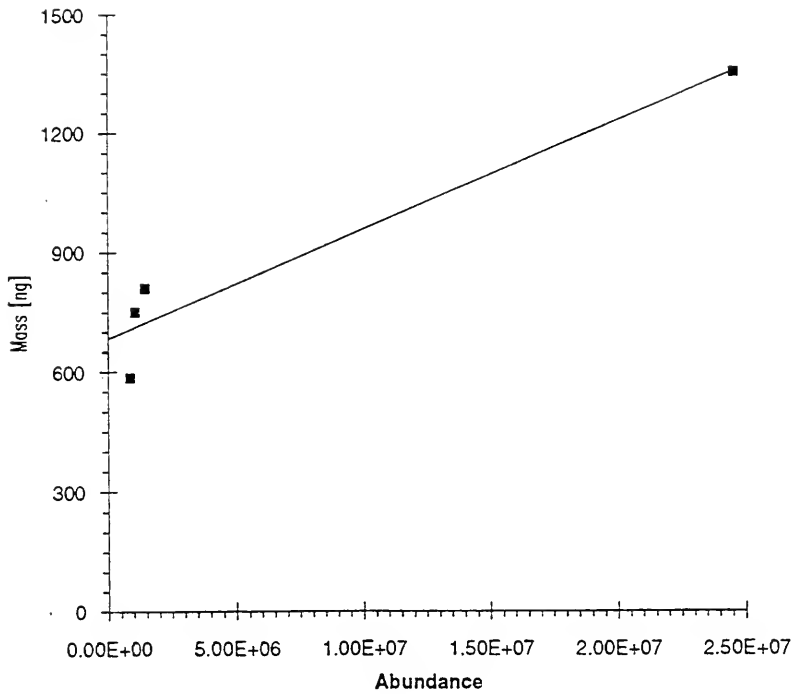
$$R^2 = 0.98$$

Experiment 1.3 - Sulfur Hexafluoride



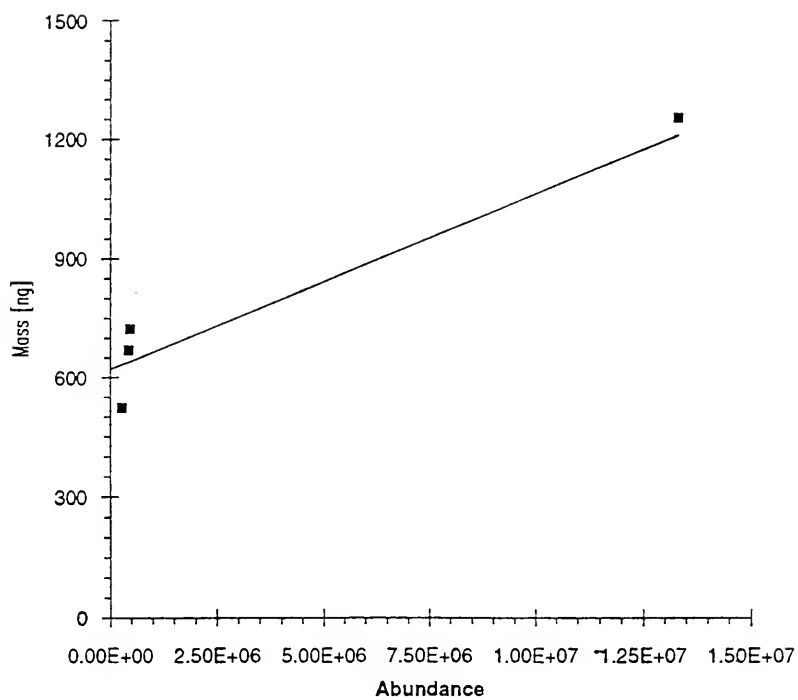
$$R^2 = 0.99$$

Experiment 2.1 - Chloroform-d



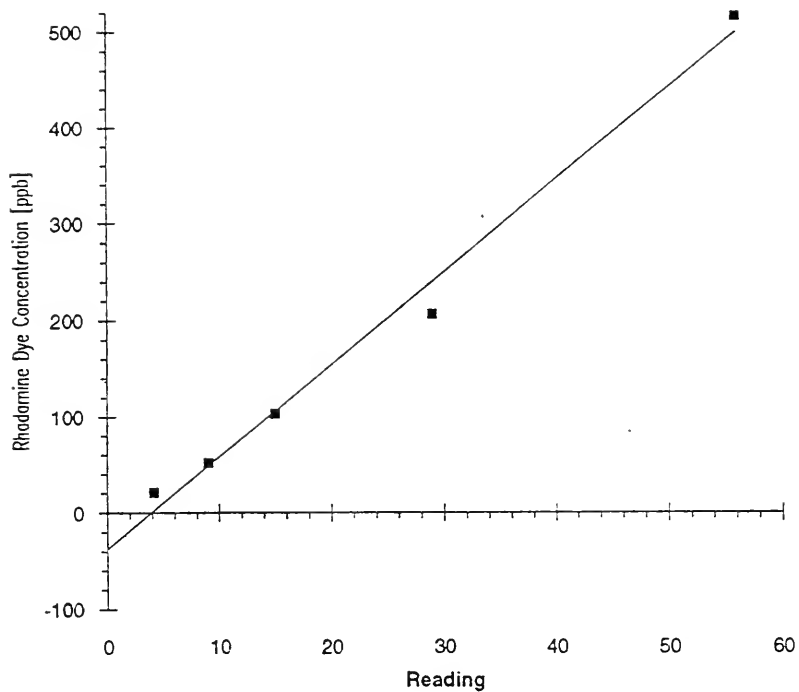
$R^2 = 0.93$

Experiment 2.1 - 1,1,1 Trichloroethane



$$R^2 = 0.92$$

Experiment 2.1 - Rhodamine Dye



$$R^2 = 0.99$$

APPENDIX B : EXPERIMENTAL RESULTS

Experiment 1.1 May 27, 1992				
VOC TRACERS				
Chloroform-d				
Liquid Samples	Abundance	Mass [ng]	Sample Volume [L]	Conc. [ug/L]
#1	2.85E+06	184.11	0.01	18.41
Gas Samples				
#1 (8 min.)	4.97E+06	420.33	1.056	0.40
#2 (5 min.)	3.31E+06	235.21	0.692	0.34
#3* (5 min.)	4.12E+06	325.88	0.642	0.51
#4* (5 min.)	2.64E+06	160.86	0.532	0.30
#5 (10 min.)	4.93E+06	415.65	1.093	0.38
(duration)				
Time Weighted Average				0.38
1,1,1-Trichloroethane				
Liquid Samples	Abundance	Mass [ng]	Sample Volume [L]	Conc. [ug/L]
#1	2.65E+06	83.45	0.01	8.35
Gas Samples				
#1 (8 min.)	6.42E+06	202.65	1.056	0.19
#2 (5 min.)	4.12E+06	129.90	0.692	0.19
#3* (5 min.)	4.70E+06	148.48	0.642	0.23
#4* (5 min.)	3.87E+06	122.00	0.532	0.23
#5 (10 min.)	6.35E+06	200.67	1.093	0.18
(duration)				
Time Weighted Average				0.20
RHODAMINE DYE TESTS				
System Hydrodynamics				
Spectrofluoro.				
Sample #	Time	Reading	WW Blank	Conc. [ppb]
#1	9:50:00	1.55	1.38	0.00
#2	9:50:30	1.40	1.38	0.00
#3	9:50:50	1.60	1.38	0.00
#4	9:51:15	2.15	1.38	0.00

#5	9:51:40	7.75	1.38	45.4
#6	9:52:10	9.70	1.38	61.8
#7	9:52:35	7.60	1.38	44.1
#8	9:53:00	4.75	1.38	20.1
#9	9:53:25	3.75	1.38	11.7
#10	9:53:50	2.90	1.38	4.57
#11	9:54:12	2.15	1.38	0.00
#12	9:54:27	1.70	1.38	0.00
#13	9:54:40	1.85	1.38	0.00
#14	9:54:54	1.80	1.38	0.00
#15	9:55:08	1.70	1.38	0.00
Wastewater Flow Rate				
#1	26:00	6.65	1.38	36.1
#2	27:00	7	1.38	39.1
#3	28:00	8.3	1.38	50
#4	29:00	7.15	1.38	40.3
			Average	41.4
			Wastewater Flow Rate [m3/sec]	0.17
SULFUR HEXAFLUORIDE (SF6)				
Sample	Abund.	Ambient Air	Mass [mg]	Conc. [mg/ml]
#1	3.35E+07	2.06E+05	5.47E-06	5.47E-04
#2	3.37E+07	2.06E+05	5.51E-06	5.51E-04
#3	2.86E+07	2.06E+05	4.62E-06	4.62E-04
#4	3.24E+07	2.06E+05	5.28E-06	5.28E-04
#5	3.19E+07	2.06E+05	5.19E-06	5.19E-04
			Average	5.21E-04
			Gas Flow Rate [m3/sec]	0.042
TEMPERATURE, pH, AND DISSOLVED OXYGEN MEASUREMENTS				
	Wastewater	Sewer Gas		Dissolved
	Temperature	Temperature	pH	Oxygen

	[C]	[C]		[mg/L]
Reading #1	15.7	18.7	8.3	1.0
Reading #2	15.6	24.4	7.8	1.6
TOTAL SUSPENDED SOLIDS				
	TSS [mg/L]			
Reading #1	164			
Reading #2	139			
Reading #3	148			
Reading #4	139			
* Duplicate gas samples				

Experiment 1.2 June 9, 1992				
VOC TRACERS				
Chloroform-d				
Liquid Samples	Abundance	Mass [ng]	Sample Volume [L]	Conc. [ug/L]
#1	8.89E+05	92.49	0.01	9.25
#2	1.29E+06	135.52	0.01	13.55
#3	1.64E+06	172.29	0.01	17.23
#4	1.30E+06	136.15	0.01	13.62
			Average	13.41
Gas Samples				
#1 (8 min.)	1.57E+06	164.91	1.056	0.16
#2 (6 min.)	1.95E+06	204.72	0.854	0.24
#3* (7 min.)	3.01E+06	317.11	0.952	0.33
#4* (7 min.)	2.82E+06	296.95	0.716	0.41
#5 (11 min.)	2.72E+06	286.75	1.151	0.25
(duration)				
		Time Weighted Average		0.25
1,1,1-Trichloroethane				
Liquid Samples	Abundance	Mass [ng]	Sample Volume [L]	Conc. [ug/L]
#1	5.45E+05	42.78	0.01	4.28
#2	6.95E+05	52.69	0.01	5.27
#3	6.37E+05	48.83	0.01	4.88
#4	7.32E+05	55.10	0.01	5.51
			Average	4.99
Gas Samples				
#1 (8 min.)	6.27E+05	48.20	1.056	0.05
#2 (6 min.)	5.89E+05	45.69	0.854	0.05
#3* (7 min.)	9.36E+05	68.57	0.952	0.07
#4* (7 min.)	1.02E+06	74.18	0.716	0.10
#5 (11 min.)	8.71E+05	64.28	1.151	0.06
(duration)				
		Time Weighted Average		0.06

RHODAMINE DYE TESTS				
System Hydrodynamics				
	Spectrofluoro.			
Sample #	Time	Reading	WW Blank	Conc. [ppb]
#1	13:35:30	1.25	1.28	0.00
#2	13:35:36	1.3	1.28	0.00
#3	13:35:42	1.2	1.28	0.00
#4	13:35:48	1.3	1.28	0.00
#5	13:35:54	1.4	1.28	0.00
#6	13:36:00	1.3	1.28	0.00
#7	13:36:06	1.2	1.28	0.00
#8	13:36:12	1.25	1.28	0.00
#9	13:36:18	1.3	1.28	0.00
#10	13:36:24	1.4	1.28	0.00
#11	13:36:30	1.4	1.28	0.00
#12	13:36:36	1.3	1.28	0.00
#13	13:36:42	1.25	1.28	0.00
#14	13:36:48	1.5	1.28	0.00
#15	13:36:54	1.5	1.28	0.00
#16	13:37:00	1.5	1.28	0.00
#17	13:37:06	1.8	1.28	0.00
#18	13:37:12	2.5	1.28	0.45
#19	13:37:18	2.5	1.28	0.45
#20	13:37:24	2.8	1.28	2.91
#21	13:37:30	3.4	1.28	7.82
#22	13:37:36	4.3	1.28	15.19
#23	13:37:42	4.9	1.28	20.11
#24	13:37:48	5.7	1.28	26.66
#25	13:37:54	6.55	1.28	33.62
#26	13:38:00	8.05	1.28	45.91
#27	13:38:06	9.6	1.28	58.60
#28	13:38:12	10.5	1.28	65.97
#29	13:38:18	11.5	1.28	74.16
#30	13:38:24	12	1.28	78.26
#31	13:38:30	13	1.28	86.45
#32	13:38:36	14.5	1.28	98.73
#33	13:38:42	14.5	1.28	98.73
#34	13:38:48	15	1.28	102.83

#35	13:38:54	15	1.28	102.83
#36	13:39:00	16	1.28	111.02
#37	13:39:06	17	1.28	119.21
#38	13:39:12	17	1.28	119.21
#39	13:39:18	17.5	1.28	123.30
#40	13:39:24	18	1.28	127.40
Wastewater Flow Rate				
#1	26:00	17.5	1.28	123.30
#2	27:00	18	1.28	127.40
#3	28:00	19.5	1.28	139.68
#4	29:00	15	1.28	102.83
			Average	123.30
		Wastewater Flow Rate [m3/sec]		0.071
SULFUR HEXAFLUORIDE (SF6)				
Sample	Abund.	Ambient Air	Mass [mg]	Conc. [mg/ml]
#1	1.75E+07	1.87E+05	3.84E-06	3.84E-04
#2	1.62E+07	1.87E+05	3.57E-06	3.57E-04
#3	1.50E+07	1.87E+05	3.32E-06	3.32E-04
#4	1.10E+07	1.87E+05	2.53E-06	2.53E-04
#5	1.35E+07	1.87E+05	3.02E-06	3.02E-04
			Average	3.26E-04
		Gas Flow Rate [m3/sec]		0.034
TEMPERATURE, pH, AND DISSOLVED OXYGEN MEASUREMENTS				
	Wastewater	Sewer Gas		Dissolved
	Temperature	Temperature	pH	Oxygen
	[C]	[C]		[mg/L]
Reading #1	15.8	18.1	9.3	2.7
Reading #2	16.7	17.8	9.0	2.7

TOTAL SUSPENDED SOLIDS		CONDUCTIVITY	
	TSS [mg/L]		Conductivity
Reading #1	186		[uS]
Reading #2	199		1460
Reading #3	139		
Reading #4	140		
* Duplicate gas samples			

Experiment 1.3 July 2, 1992				
VOC TRACERS				
Chloroform-d				
Liquid Samples	Abundance	Mass [ng]	Sample Volume [L]	Conc. [ug/L]
#1	5.41E+06	439.16	0.01	43.92
#2	7.01E+06	549.58	0.01	54.96
			Average	49.44
Gas Samples				
#1 (10 min)	2.79E+05	95.15	0.620	0.15
#2 (8 min.)	2.44E+05	91.29	0.656	0.14
#3 (10 min)	2.81E+05	95.40	0.629	0.15
#4 (9 min.)	6.79E+05	138.80	0.874	0.16
(duration)				
			Time Weighted Average	0.15
1,1,1-Trichloroethane				
Liquid Samples	Abundance	Mass [ng]	Sample Volume [L]	Conc. [ug/L]
#1	3.70E+06	372.53	0.01	37.25
#2	4.96E+06	471.85	0.01	47.19
			Average	42.22
Gas Samples				
#1 (10 min)	6.01E+05	128.21	0.620	0.21
#2 (8 min.)	1.12E+06	168.83	0.656	0.26
#3 (10 min)	9.18E+05	153.17	0.629	0.24
#4 (9 min.)	1.55E+06	203.34	0.874	0.23
(duration)				
			Time Weighted Average	0.23
RHODAMINE DYE TESTS				
System Hydrodynamics				
		Spectrofluoro.		
Sample #	Time	Reading	WW Blank	Conc. [ppb]

#1	14:26:20	0.00	0.00	0.20
#2	14:26:26	0.00	0.00	0.20
#3	14:26:32	0.00	0.00	0.20
#4	14:26:38	0.00	0.00	0.20
#5	14:26:44	0.00	0.00	0.20
#6	14:26:50	0.00	0.00	0.20
#7	14:26:56	0.00	0.00	0.20
#8	14:27:02	0.00	0.00	0.20
#9	14:27:08	2.65	0.00	26.3
#10	14:27:14	2.45	0.00	24.3
#11	14:27:20	3.00	0.00	29.7
#12	14:27:26	5.00	0.00	49.4
#13	14:27:32	9.40	0.00	92.7
#14	14:27:38	11.5	0.00	113
#15	14:27:44	12.0	0.00	118
#16	14:27:50	12.5	0.00	123
#17	14:27:56	13.5	0.00	133
#18	14:28:02	14.5	0.00	143
#19	14:28:08	14.5	0.00	143
#20	14:28:14	15.0	0.00	148
#21	14:28:20	15.5	0.00	153
#22	14:28:26	15.0	0.00	148
#23	14:28:32	14.0	0.00	138
#24	14:28:38	13.0	0.00	128
#25	14:28:44	10.0	0.00	98.6
#26	14:28:50	9.10	0.00	89.7
#27	14:28:56	7.20	0.00	71.0
#28	14:29:02	5.40	0.00	53.3
#29	14:29:08	2.40	0.00	23.8
#30	14:29:14	2.55	0.00	25.3
#31	14:29:20	1.50	0.00	15.0
#32	14:29:26	2.30	0.00	22.8
#33	14:29:32	0.90	0.00	9.06
#34	14:29:38	0.40	0.00	4.14
#35	14:29:44	1.30	0.00	13.0
#36	14:29:50	0.60	0.00	6.10
#37	14:29:56	0.20	0.00	2.17
#38	14:30:02	0.20	0.00	2.17
#39	14:30:08	0.20	0.00	2.17
#40	14:30:14	0.20	0.00	2.17

Wastewater Flow Rate				
#1	26:00	8.85	0.00	87.28
#2	27:00	10.0	0.00	98.60
#3	28:00	10.0	0.00	98.60
#4	29:00	12.0	0.00	118.28
			Average	100.69
		Wastewater Flow Rate [m3/sec]		0.10
SULFUR HEXAFLUORIDE (SF6)				
Sample	Abund.	Ambient Air	Mass [mg]	Conc. [mg/ml]
#1	1.34E+07	5.03E+05	2.55E-06	2.55E-04
#2	1.20E+07	5.03E+05	2.27E-06	2.27E-04
#3	1.40E+07	5.03E+05	2.67E-06	2.67E-04
#4	1.38E+07	5.03E+05	2.63E-06	2.63E-04
#5	1.30E+07	5.03E+05	2.47E-06	2.47E-04
			Average	2.52E-04
		Gas Flow Rate [m3/sec]		0.175
TEMPERATURE, pH, AND DISSOLVED OXYGEN MEASUREMENTS				
	Wastewater	Sewer Gas		Dissolved
	Temperature	Temperature	pH	Oxygen
	[C]	[C]		[mg/L]
Reading #1	17.0	17.7	8.6	0.22
Reading #2	17.0	N/A	N/A	0.24
TOTAL SUSPENDED SOLIDS			CONDUCTIVITY	
	TSS [mg/L]		Conductivity	
Reading #1	293		[uS]	
Reading #2	290		1632	
Reading #3	264			

Reading #4	258			
Reading #5	146			
Reading #6	146			
Reading #7	154			
Reading #8	144			



CANVIRO
Analytical Laboratories Ltd.

SCHOOL OF ENGINEERING
UNIVERSITY OF GUELPH
THORNBOROUGH BUILDING
GUELPH, ONTARIO N1G 2W1
Attn: MS. ARLENE WHITMORE

Date Received: 07/07/92
Date Reported: 07/22/92
Work Order: 92-07-051
Category:

Work ID: TOC'S
P O # : 011044

Test	Units	EXP.#3 W.W. SAMPLE #1 Sample 01 07/02/92	EXP.#3 W.W. SAMPLE #2 Sample 02 07/02/92	EXP.#3 W.W. SAMPLE #3 Sample 03 07/02/92	EXP.#3 W.W. SAMPLE #4 Sample 04 07/02/92
Total Organic Carbon	mg/L	65.7	62.0	54.6	57.3

Certified By:

THE LIABILITY OF CANVIRO ANALYTICAL LABORATORIES LTD., OR ASSOCIATED
FIRMS EXTENDS ONLY TO THE PRICE OF THE ANALYSIS.

Experiment 2.1 July 21, 1992				
VOC TRACERS				
Chloroform-d				
Liquid Samples	Abundance	Mass [ng]	Sample Volume [L]	Conc. [ug/L]
#1	9.01E+06	928.56	0.01	92.86
#2	1.01E+07	958.49	0.01	95.85
			Average	94.35
Gas Samples				
#1* (10 min)	8.01E+06	901.45	0.556	1.62
#2* (8 min.)	1.08E+06	712.87	0.234	3.05
(duration)				
		Time Weighted Average		2.33
1,1,1-Trichloroethane				
Liquid Samples	Abundance	Mass [ng]	Sample Volume [L]	Conc. [ug/L]
#1	8.08E+06	975.41	0.01	97.54
#2	8.62E+06	999.16	0.01	99.92
			Average	98.73
Gas Samples				
#1* (10 min)	1.34E+07	1206.67	0.556	2.17
#2* (8 min.)	3.74E+06	784.71	0.234	3.35
(duration)				
		Time Weighted Average		2.76
RHODAMINE DYE TESTS				
System Hydrodynamics				
Spectrofluoro.				
Sample #	Time	Reading	WW Blank	Conc. [ppb]
#1	11:21:00	2.10	4.78	0.00
#2	11:12:15	2.60	4.78	0.00
#3	11:21:30	9.20	4.78	4.80
#4	11:21:45	18.50	4.78	93.8

#5	11:22:00	26.00	4.78	166
#6	11:22:15	26.00	4.78	166
#7	11:22:30	20.50	4.78	113
Wastewater Flow Rate				
#1	7:00	31.00	4.78	213
#2	8:00	30.5	4.78	209
#3	9:00	30.5	4.78	209
#4	10:00	31.0	4.78	213
			Average	211
		Wastewater Flow Rate [m3/sec]		0.020
TEMPERATURE, pH, AND DISSOLVED OXYGEN MEASUREMENTS				
	Wastewater	Sewer Gas		Dissolved
	Temperature	Temperature	pH	Oxygen
	[C]	[C]		[mg/L]
Reading #1	18.9	23.2	8.4	4.7
TOTAL SUSPENDED SOLIDS			CONDUCTIVITY	
	TSS [mg/L]		Conductivity	
Reading #1	117		[uS]	
Reading #2	110		1580	
Reading #3	98			
Reading #4	113			
*Duplicate gas samples				

UNCERTAINTY ANALYSIS

$$-K = \frac{Q_v C_g}{\left(C_e - \frac{C_g}{H_c}\right) A} \quad \text{Equation (14)}$$

Differentiating Eqn. (14) with respect to all other variables in the equation allows an estimate of the error associated with K to be developed:

$$\begin{aligned} -\Delta K &\cong \frac{\partial K}{\partial Q_v} \Delta Q_v + \frac{\partial K}{\partial C_e} \Delta C_e + \frac{\partial K}{\partial C_g} \Delta C_g + \frac{\partial K}{\partial H_c} \Delta H_c + \frac{\partial K}{\partial A} \Delta A \\ &\cong \underbrace{\left[\frac{C_g}{\left(C_e - \frac{C_g}{H_c}\right) A} \right] \Delta Q_v}_{\text{Term I}} - \underbrace{\left[\frac{Q_v C_g A}{\left[\left(C_e - \frac{C_g}{H_c}\right) A\right]^2} \right] \Delta C_e}_{\text{Term II}} \\ &\quad + \underbrace{\left[\frac{Q_v}{\left(C_e - \frac{C_g}{H_c}\right) A} - \frac{Q_v C_g A}{\left[\left(C_e - \frac{C_g}{H_c}\right) A\right]^2 H_c} \right] \Delta C_g}_{\text{Term III}} \\ &\quad - \underbrace{\left[\frac{Q_v C_g}{\left[\left(C_e - \frac{C_g}{H_c}\right) A\right]^2 \left(\frac{C_g}{H_c^2} A\right)} \right] \Delta H_c}_{\text{Term IV}} - \underbrace{\left[\frac{Q_v C_g \left(C_e - \frac{C_g}{H_c}\right)}{\left[\left(C_e - \frac{C_g}{H_c}\right) A\right]^2} \right] \Delta A}_{\text{Term V}} \end{aligned}$$

Accompanying spreadsheets show calculation of % Error = $\frac{\Delta K}{K} \times 100\%$.
(overall uncertainty) for each experiment and tracer compound.

<i>Experiment 1.1 - Uncertainty Analysis</i>										
Chloroform-d										
K	Qv	Cl	Cg	Hc	A					
[m/hr]	[m3/hr]	[ug/L]	[ug/L]	[-]	[m2]					
0.028	155	18	0.38	0.09	130					
Delta K	Term I	Delta Qv	Term II	Delta Cl	Term III	Delta Cg	Term IV	Delta Hc	Term V	Delta A
[m/hr]		[m3/hr]		[ug/L]		[ug/L]		[-]		[m2]
0.034	0.000211	26.3	0.00236	4.32	0.060406	0.1634	0.106214	0.013	0.000252	26
										% Error
										118.5481
1,1,1-Trichloroethane										
K	Qv	Cl	Cg	Hc	A					
[m/hr]	[m3/hr]	[ug/L]	[ug/L]	[-]	[m2]					
0.028	155	8.4	0.2	0.45	130					
Delta K	Term I	Delta Qv	Term II	Delta Cl	Term III	Delta Cg	Term IV	Delta Hc	Term V	Delta A
[m/hr]		[m3/hr]		[ug/L]		[ug/L]		[-]		[m2]
0.030	0.000194	26.3	0.00377	1.71	0.141647	0.086	0.003693	0.0675	0.000231	26
										% Error
										105.9268

Experiment 1.2 - Uncertainty Analysis										
Chloroform-d										
K	Qv	Cl	Cg	Hc	A					
[m/hr]	[m3/hr]	[ug/L]	[ug/L]	[-]	[m2]					
0.025	130	13	0.27	0.09	111					
Delta K	Term I	Delta Qv	Term II	Delta Cl	Term III	Delta Cg	Term IV	Delta Hc	Term V	Delta A
[m/hr]		[m3/hr]		[ug/L]		[ug/L]		[-]		[m2]
0.032	0.000239	22	0.003056	3.12	0.082665	0.116	0.091873	0.0135	0.000279	22
										% Error
										126.3695
1,1,1-Trichloroethane										
K	Qv	Cl	Cg	Hc	A					
[m/hr]	[m3/hr]	[ug/L]	[ug/L]	[-]	[m2]					
0.015	130	5	0.061	0.46	111					
Delta K	Term I	Delta Qv	Term II	Delta Cl	Term III	Delta Cg	Term IV	Delta Hc	Term V	Delta A
[m/hr]		[m3/hr]		[ug/L]		[ug/L]		[-]		[m2]
0.015	0.000113	22	0.003002	1.2	0.233134	0.0262	0.000849	0.069	0.000132	22
										% Error
										98.54825

Experiment 2.1 - Uncertainty Analysis										
Chloroform-d										
K exp.	Qv	Cl	Cg	Hc	Term III	Delta Cg	Term IV	Delta Hc	Term V	Delta A
[m/hr]	[m3/hr]	[ug/L]	[ug/L]	[.]	[m2]	[ug/L]		[.]		[m2]
0.15	108	94	2.3	0.11	21	0.989	0.427456	0.0165	0.007539	4.3
Delta K	Term I	Delta Qv	Term II	Delta Cl	Term III	Delta Cg	Term IV	Delta Hc	Term V	Delta A
[m/hr]		[m3/hr]		[ug/L]		[ug/L]		[.]		[m2]
0.16	0.001484	18.4	0.0022	22.56	0.049482	0.989	0.427456	0.0165	0.007539	4.3
										% Error
										111.4765
1,1,1-Trichloroethane										
K exp.	Qv	Cl	Cg	Hc	Term III	Delta Cg	Term IV	Delta Hc	Term V	Delta A
[m/hr]	[m3/hr]	[ug/L]	[ug/L]	[.]	[m2]	[ug/L]		[.]		[m2]
0.15	108	99	2.8	0.53	21	1.2	0.016455	0.0795	0.007139	4.3
Delta K	Term I	Delta Qv	Term II	Delta Cl	Term III	Delta Cg	Term IV	Delta Hc	Term V	Delta A
[m/hr]		[m3/hr]		[ug/L]		[ug/L]		[.]		[m2]
0.16	0.001406	18.4	0.001621	23.76	0.051135	1.2	0.016455	0.0795	0.007139	4.3
										% Error
										103.5446

APPENDIX C : CONFERENCE PAPER

Examining Gas-Liquid Mass Transfer of Volatile and
Semi-Volatile Organic Compounds Along Sewer Reaches

Arlene Whitmore, Richard L. Corsi, Jennifer Shepherd
School of Engineering
University of Guelph
Guelph, Ontario, Canada N1G 2W1

Doug Thompson
Enviromega Ltd.
P.O. Box 1249
Burlington, Ontario, Canada L7R 4L8

INTRODUCTION

In recent years, the fate of volatile and semi-volatile organic compounds (VOCs and semi-VOCs) in wastewater has become a concern for many municipalities and regulatory agencies. These concerns stem from the extensive use of VOCs and semi-VOCs, and the health risks associated with their presence. Prolonged exposure to low concentrations of many VOCs and semi-VOCs, e.g. benzene, ethylene dibromide, tetrachloroethene and vinyl chloride, can lead to significantly increased cancer risk.¹

The fate of VOCs and semi-VOCs in wastewater collection systems is governed by a complex series of mechanisms, including adsorption/desorption to/from solid particles, absorption in immiscible liquids, aerobic and/or anaerobic biodegradation and gas-liquid partitioning. Although all of these mechanisms play a role in either transporting or transforming organic compounds, their relative importance will depend on individual sewer and wastewater characteristics. Determining factors include physicochemical properties of individual VOCs or semi-VOCs, degree of turbulent mixing, presence of surface films and suspended solids, degree of saturation of the sewer headspace, and wastewater temperature.

Analysis of an entire wastewater collection system would involve a vast network of sewer lines, junctions and pump stations. As a first step, analysis of uniform reaches has been undertaken. This paper presents the results of initial monitoring in an industrialized sewer in Toronto, and examines the impact of numerous factors on overall mass transfer along uninterrupted sewer lines.

LEVELS OF VOCS IN SEWERS

Few studies have reported levels of organic pollutants in sewer environments. Levins et al.² monitored aqueous concentrations of priority pollutants in the wastewater collection systems of Atlanta, Cincinnati, Hartford, and St. Louis. A total of 11 residential, 10 commercial and 5 industrial sewers were monitored, in addition to tap water and treatment plant influent. Over all, thirteen VOCs were detected. Average concentrations for individual VOCs in residential and commercial sewers were 10 µg/L and 25 µg/L, respectively. Concentrations in sewers accepting industrial discharges ranged from less than 1 µg/L to 100 µg/L, with average concentrations of ethylbenzene, tetrachloroethene, toluene, 1,1,1-trichloroethane, and trichloroethene exceeding 50 µg/L.

Huang et al.³ collected sewer off-gas from a main interceptor to the Sacramento Main Treatment Plant in order to evaluate the effectiveness of activated carbon adsorption for sewer odour control. All samples were analyzed by GC/FID to determine total hydrocarbon concentrations. The results of four sampling events indicated the presence of 59, 531, 76, and 13 ppm total hydrocarbon. Across the samples, compounds with 8 or more carbon atoms prevailed. Reid and McEvoy⁴ examined sewer atmospheres in London, England. In a sewer receiving relatively small amounts of industrial effluent, gaseous benzene, trichloroethene, and toluene levels were <0.5, <0.5 and 5 parts per million by volume (ppmV), respectively. However, in a sewer reported to contain a high level of industrial wastewater, gaseous concentrations of these same three compounds reached 52, 116, and 170 ppmV. Semi-volatile organic compounds were also detected within this second sewer atmosphere. Levels of 1,4-dichlorobenzene were reported to be 4 ppmV, while levels of 1,2-dichlorobenzene reached 14 ppmV.

As part of the overall research effort described in this paper, field monitoring was

completed in a heavily industrialized municipal sewer in Toronto, Ontario. Although there was apparent significant ventilation of the sewer reach (e.g. several manholes were well-perforated and observed to have physically detectable outflows), concentrations of many VOCs during initial monitoring events were extremely high. The results of stainless steel canister samples, analyzed using a Hewlett-Packard model 5890 gas chromatograph and 5970 quadrupole mass spectrometer, are shown in Table I.

TABLE I. Sewer atmosphere analysis - site 1.

Compound	Concentration [$\mu\text{g}/\text{m}^3$]	Concentration [ppbV at 20°C]	Method Detection Limit [$\mu\text{g}/\text{m}^3$] *
Benzene	28	9	0.4
Chlorobenzene	ND	ND	1.6
Chloroform	760	153	2.8
1,4-Dichlorobenzene	ND	ND	2.0
Dichloromethane	269	76	6.8
Ethylbenzene	17 000	4 000	0.6
Tetrachloroethene	5 000	700	1.4
Toluene	168 000	44 000	1.4
1,1,1-Trichloroethane	3 000	500	2.0
Trichloroethene	242	44	1.4
m/p-Xylenes	84 000	19 000	3.0
o-Xylene	51 000	12 000	1.2
2-Ethyltoluene	81 000	16 000	0.8
3-Ethyltoluene	195 000	39 000	1.4
4-Ethyltoluene	115 000	23 000	1.0
1,2,4-Trimethylbenzene	174 000	35 000	0.6
1,3,5-Trimethylbenzene	94 000	19 000	0.6

* = estimated MDLs based upon 500ml injection volume

ND = not detected

Gaseous concentrations of several aromatic VOCs were particularly high, suggesting significant aqueous discharges, high mass transfer coefficients, or both. Research is currently underway to couple VOC and gas flow measurements for quantifying emission rates from the aforementioned sewer reach.

FACTORS AFFECTING MASS TRANSFER IN SEWERS

Mass transfer across a gas-liquid boundary is often described by the equation:

$$N = K A \left(C_l - \frac{C_g}{H_c} \right) \quad (1)$$

Where N = Mass transfer rate, [M/T]

K = Overall mass transfer coefficient, [L/T]

- A = Interfacial area, $[L^2]$
 C_l = Mass concentration in liquid phase, $[M/L^3]$
 C_g = Mass concentration in gas phase, $[M/L^3]$
 H_c = Dimensionless Henry's Law constant $[-]$.

The overall mass transfer coefficient used in Equation (1) may be subdivided into its contributing components:

$$K = \frac{1}{\frac{1}{k_l} + \frac{1}{k_g H_c}} \quad (2)$$

- Where K = Overall mass transfer coefficient, $[L/T]$
 k_l = Liquid phase mass transfer coefficient, $[L/T]$
 k_g = Gas phase mass transfer coefficient, $[L/T]$
 H_c = Dimensionless Henry's Law constant $[-]$.

Mass transfer from wastewater to sewer gas is also described by Equations (1) & (2). However, there are numerous factors that must be assessed.

Sewer line characteristics affect mass transfer of VOCs and semi-VOCs because variables within Equations (1) & (2) are influenced by changes in geometry and flow. The relative depth of wastewater flow along the sewer channel affects the surface area available for mass transfer and the total volume of headspace above the wastewater surface. In addition, the relative depth of flow influences the liquid phase mass transfer coefficient because it alters the surface renewal rate and the degree of turbulent mixing within the wastewater. Pipe diameter also affects surface area and overall gas volume. Sewer channel slope and relative roughness affect uniform flow characteristics. Reaches with steep slopes are expected to exhibit higher mass transfer coefficients due to higher mean wastewater velocities and increased turbulent mixing.

The properties of constituents within the wastewater are of particular importance. Volatile organic compounds possess extremely high Henry's law constants ($H_c > 0.1$), while semi-volatile organic compounds possess only moderate Henry's law constants ($0.1 > H_c > 1 \times 10^{-5}$). This drop in Henry's law constant substantially reduces the product $k_g H_c$ in Equation (2), thus potentially reducing the overall mass transfer coefficient by several orders of magnitude.

Variables within Equations (1) & (2) are also influenced by physical and chemical characteristics of wastewater. Such characteristics include wastewater temperature and the presence or absence of surfactants. Warmer wastewater temperatures augment the liquid phase mass transfer coefficient, k_l , the gas phase mass transfer coefficient, k_g , and the Henry's law constant, H_c . Surfactants act to increase surface tension and, depending on the situation, can either reduce or increase the interfacial area available for mass transfer, and potentially retard mass transfer at the wastewater-air interface.⁵ Finally, the presence of solids or attached or suspended microorganisms can reduce gas-liquid mass transfer by direct competition for VOC mass, and subsequent reductions in C_l , through solids adsorption or biodegradation. These competing removal mechanisms are not considered in this paper.

Ventilation affects overall mass transfer between liquid and gas because of its impact on the

gas-phase concentration, C_g . In well ventilated systems, gas concentrations typically remain small, diluted by incoming fresh air. In poorly ventilated systems gas concentrations can become elevated, as mass is allowed to accumulate in the head space. The diversity and complexity of wastewater collection systems have been major obstacles to successfully quantifying factors that affect their ventilation. Most systems are naturally ventilated, although some have been artificially ventilated, generally to prevent H_2S formation. For those naturally ventilated systems, the number of openings which allow for gas exchange between sewer and ambient atmospheres affects the degree of ventilation. Ventilation rates are expected to be highest in combined sanitary/storm systems and in residential areas with many house vents and short distances between manhole covers. Ventilation rates are expected to be lowest for large sanitary interceptors.⁶

MASS TRANSFER COEFFICIENTS

Of all the variables presented in Equations (1) and (2), the mass transfer coefficients, K , k_l , and k_g remain the most difficult to routinely quantify. Numerous models have been developed to predict mass transfer coefficients. The majority have dealt with the transfer of oxygen in clean water systems. A conceptual model for reaeration of natural streams was developed by O'Connor and Dobbins.⁷ This was followed by other models by Cadwallader and McDonnell⁸ and Tsivoglou and Neal.⁹ Parkhurst and Pomeroy¹⁰ developed one of the only models for mass transfer within sewer environments. Their semi-empirical model deals with the transfer of oxygen along sewer reaches and is based on field experiments conducted in 12 operating sewers. Although the model predicts reaeration based on a number of parameters, it does not account for biological oxygen consumption. The authors chose to circumvent the problem of biological activity by shock loading the experimental sewer reaches with caustic soda 24 hours prior to testing, and feeding hypochlorite into the wastewater during each test. According to their model

$$k_{l0} = 2.67 \times 10^{-4} (1 + 0.17F^2) \gamma (SU)^{3/8} \quad (3)$$

Where F = Froude number [-]

γ = temperature correction factor [-]

k_{l0} = oxygen transfer coefficient [m/s]

S = slope of the energy gradient [m/m]

U = mean velocity of the wastewater [m/s].

Predictions of liquid phase oxygen mass transfer coefficients allow subsequent estimation of liquid-phase mass transfer coefficients for other compounds using the relationship

$$\Psi = \left\{ \frac{D_{li}}{D_{lj}} \right\}^n = \frac{k_{li}}{k_{lj}} \quad (4)$$

Where D_{li} = Liquid molecular diffusion coefficient for compound i [L^2/T]

D_{lj} = Liquid molecular diffusion coefficient for compound j [L^2/T]

k_{li} = Liquid-phase mass transfer coefficient for compound i [L/T]

k_{lj} = Liquid-phase mass transfer coefficient for compound j [L/T]

n = Exponent which varies from 0.5 to 1.0 depending on the degree of liquid agitation.

This relationship proves valuable for VOCs because measured values of Ψ for VOCs and oxygen in well-mixed systems are generally close to 0.6 and, for $H_C > 0.1$, the overall mass transfer coefficient can be approximated by k_l . For compounds with $H_C < 0.1$, resistance to gas phase mass transfer can not be ignored. Values of k_g for enclosed channels are not available in the literature, and thus this study focuses on compounds with $H_C > 0.1$.

Corsi⁶ used Equations (3) and (4) to predict mass transfer coefficients for chloroform ($H_C = 0.14$) along two municipal sewer reaches. He found that the predicted coefficients were within $\pm 33\%$ of experimentally determined mass transfer coefficients. Jensen and Hvitrved-Jacobsen¹¹ investigated the use of radiotracers to obtain oxygen transfer coefficients. They also found that Equation (3) complemented their experimentally determined oxygen transfer coefficients. For the gravity sewer line studied, Equation (3) predicted a reaeration coefficient of 0.43 h^{-1} , compared with measured values of 0.50 to 0.52 h^{-1} .

SEWER REACH SIMULATIONS

Individual sewer reach simulations were carried out using CORAL (Collection system Organic Release ALgorithm). This is a one-dimensional, two-phase model designed to predict gas-liquid mass transfer along sewer reaches. Mass transfer estimates are based on Equations (3) and (4). The computational solution treats both gaseous and liquid phases of the sewer line as series of n continuous flow, stirred tank reactors (CFSTRs). It accommodates variable liquid and gas flow rates (and interfacial areas), variable air exhaust and intake patterns, and continuous, slug or intermittent discharges. Biodegradation and sorption losses are assumed to be negligible. Corsi⁶ evaluated the CORAL model using data from 4 field experiments. In two of the cases, CORAL overpredicted experimental values by 18% and 28%. In the remaining cases, CORAL underpredicted experimental values by 17% and 25%. Differences of these magnitudes are considered quite adequate given other uncertainties in sewer, wastewater and ventilation characteristics.

For this study, sewer reach simulations were completed to evaluate the "half-length" associated with various scenarios. In the context of this paper, half-length represents the length of sewer line over which one-half of the VOC mass, discharged in the aqueous phase, is expected to be lost through emissions to the ambient atmosphere. For all simulations, a continuous discharge of $100 \mu\text{g/l}$ at the upstream end of the sewer reach was assumed. Wastewater temperature was held constant at 20°C , and a channel roughness coefficient of 0.013 was applied. A summary of other sewer input parameters and the resulting half-lengths is provided in Table II.

For all simulations, sewer reaches were assumed to be flowing one-quarter full. Small (0.5 m) and large (2.0 m) pipe diameters were evaluated. Sewer channel slope was held at 0.005 m/m, while ventilation rate and Henry's law constant were varied. The two shortest half-lengths occurred along the smaller diameter reach, under well-ventilated conditions. The 2.0 m pipe in Simulation #8 exhibited a half length that was 38% greater than that in Simulation #3. This was true despite the fact that the two reaches were equally ventilated and the Henry's law constant for Simulation #8 was an order of magnitude higher.

TABLE II. CORAL input parameters and resulting half-lengths.

Simulation No.	Pipe Diameter [m]	Depth [m]	Slope [m/m]	Ventilation Rate [TuPD]	Dimensionless Henry's Law Constant	Half-Length [km]
1	0.5	0.125	0.005	0.1	0.1	>1000
2	0.5	0.125	0.005	0.1	1.0	114
3	0.5	0.125	0.005	10.0	0.1	13
4	0.5	0.125	0.005	10.0	1.0	3
5	2.0	0.5	0.005	0.1	0.1	>1000
6	2.0	0.5	0.005	0.1	1.0	295
7	2.0	0.5	0.005	10.0	0.1	43
8	2.0	0.5	0.005	10.0	1.0	18

In general, low ventilation rates and relatively high Henry's law constants combined to give half-lengths far greater than the average conveyance distance in industrial or municipal wastewater collection systems. Furthermore, increased depths of flow would result in even larger half-lengths. These model simulations suggest that relative removal of VOCs from uniform sewer reaches can be quite low. However, they do not account for stripping and subsequent emissions caused by sewer drop structures such as drop manholes. This loss mechanism is examined in a companion paper.¹²

MULTI-PARAMETER ANALYSIS

Multi-parameter analyses were completed using MATES (Multiparameter Assessment of Toxic Emissions from Sewers). MATES is an extension of CORAL. It uses the same computational solution to determine emissions along a sewer line, but re-executes the model over ranges of input parameters. The major difference between MATES and CORAL is the manner in which MATES tracks the outcome of each run. As MATES completes each run, the percentage of mass removed from the system is calculated. This percentage of mass removed from the system is then compared to a user specified fractional removal criterion. If the emissions meet or exceed this fractional removal criterion the outcome of the run is stored as a "hit" (1), otherwise a "miss" (0) is registered. Systematically, MATES steps through all combinations recording "hits" and "misses".

The MATES model allows sequential variation of the following parameters: pipe diameter, relative depth of wastewater, slope, ventilation rate, and Henry's law constant. It examines the parameters in pairs, for example, relative depth vs. ventilation rate. For every pair, a full set of runs is executed evaluating every combination of the remaining parameters. For example, in the case of relative depth versus ventilation rate, MATES could hold relative depth constant at a value 0.1 and ventilation rate constant at a value of 0.1 turnovers per day, and run through all combinations of pipe diameter, slope and Henry's law constant. Then, relative depth could be increased to 0.2, while ventilation remained at 0.1 turnovers per day, and once again all combinations of pipe diameter, slope and Henry's law constant would be evaluated. Eventually all relative depths vs. ventilation rates would be covered and the resulting output would be a frequency array, in which the total number of "hits" is expressed as a percentage of the total number of combinations attempted.

Figure 1 provides an example of the percentage of cases in which the fractional removal criterion was violated for every pairing of relative depth and ventilation rate. For example, with a relative wastewater depth of 0.2 and a ventilation rate of 10 turnovers per day, 19% of all combinations of the remaining parameters led to at least 50% removal. Other frequency arrays would be created as MATES moved on to other parameter pairs, such as pipe diameter versus relative depth.

In order to carry out its multi-parameter analysis, MATES requires a series of input values for each parameter being investigated, as well as certain fixed characteristics. The parameters and ranges of input values used in this study are presented in Table III. The resulting MATES output is presented in Figures 2, 3 & 4.

TABLE III. Ranges of input parameters for MATES analysis.

Input Parameters	Values
Pipe Diameter [m]	0.3 - 2.1
Relative Depth	0.1 - 0.7
Slope [m/m]	0.0005 - 0.04
*Ventilation Rate [TuPD]	0.1 - 100.0
Dimensionless Henry's Law Constant [-]	0.1 - 1.1
Fixed Parameters	
**Continuous Discharge [$\mu\text{g/L}$]	100
Wastewater Temperature [$^{\circ}\text{C}$]	15
Sewer Reach Length [km]	5
Relative Roughness [-]	0.014
Fractional Removal Criterion [%]	50

* TuPD = Turnovers Per Day based on total (empty) pipe volume.

** after mixing with wastewater.

Figure 2 indicates the predicted impact of relative depth of wastewater flow and ventilation rate along a 5 km reach. It illustrates several interesting points. For relative depths greater than 0.3 and ventilation rates lower than 5 turnovers per day, 50% removal will never be achieved, over the full range of diameters, slopes, and Henry's law constants considered. However, for relative depths of 0.1 and ventilation rates greater than 5 turnovers per day, 50% mass removal is predicted to occur in the majority of cases (65%). This points to a potential problem with the practice of off-hour discharges. Although off-peak discharges may improve the distribution of loads to wastewater treatment plants, they tend to take place when collection system flows are lowest and mass stripping rates are highest.

Figure 3 focuses on the impact of relative depth of wastewater flow and pipe diameter along a 5 km reach. Note that these two parameters can be combined to provide information regarding absolute depth. For example, at absolute depths of more than 0.4 m, the 50% removal criterion is never met, regardless of the pipe diameter. However, for absolute depths less than 0.4 m, the sensitivity of mass removal to depth of flow increases sharply.

Figure 4 focuses on the impact of Henry's law constant, H_c , and ventilation rate, Q_v . The degree of mass removal is highly sensitive to Henry's law constant at ventilation rates lower than

20 TuPD. However, sensitivity to Henry's law constant disappears at high ventilation rates. This is due to the diminishing value of C_g in Equation (1). Finally, comparable products of Henry's law constant and ventilation rate ($H_C Q_V$), produce comparable degrees of removal. For example, a combined ventilation rate of 20 TuPD and Henry's law constant of 0.1 ($H_C Q_V = 2.0$), lead to at least 20% mass removal in 21% of the cases run. A ventilation rate of 3.0 TuPD and Henry's law constant of 0.7 ($H_C Q_V = 2.1$), produce at least 20% mass removal in 22% of the cases run. Furthermore, a ventilation rate of 50 TuPD and Henry's law constant of 0.3 ($H_C Q_V = 15$), produce at least 20% mass removal in 57% of the cases, and a ventilation rate of 20 TuPD and Henry's law constant of 0.7 ($H_C Q_V = 14$), produce at least 20% mass removal in 55% of the cases run. This indicates that the degree of mass removal for many combinations of ventilation rates and Henry's law constants may be predicted provided that information regarding a few ventilation rates and Henry's law constants are known.

SUMMARY AND CONCLUSIONS

Significant quantities of VOCs and semi-VOCs may be found in the sewer atmospheres of highly industrialized reaches. However, these elevated concentrations alone are not indicative of high emissions. The reach must also be subject to adequate ventilation. Head space samples collected in an industrialized sewer reach in Toronto were characterized by high gaseous concentrations of several aromatic VOCs. These concentrations along with physically evident outgassing have focussed the efforts of this research on methods of coupling compound concentrations and gas flow measurements in order to quantify emission rates from several industrialized sewer reaches in Toronto.

Sewer reach simulations indicated that low ventilation rates and relatively high Henry's law constants combine to give half-lengths far greater than the average conveyance distance in industrial or municipal wastewater collection systems. These model simulations suggest that relative removal of VOCs from uniform sewer reaches can be quite low. However, they did not account for stripping and subsequent emissions caused by sewer drop structures.

Multi-parameter analyses provided insight into conditions which lead to significant VOC mass removal along a 5 km reach. Generally, these conditions included small pipe diameters, low relative depths, and high ventilation rates. This approach to sewer emissions estimations could simplify the screening of wastewater collection systems, allowing efforts to be focussed on reaches that have high emissions potential.

REFERENCES

1. J. Seinfeld, Atmospheric Chemistry and Physics of Air Pollution, John Wiley and Sons Inc., New York, 1986, pp 60-65.
2. P. Levins et al., Sources of Toxic Pollutants Found in Influent to Sewage Treatment Plants 6. Integrated Interpretation, EPA/440/4-81/007, U.S. Environmental Protection Agency, Washington, D.C., 1979.
3. J.Y.C. Huang, G.E. Wilson and T.W. Schroepfer, "Evaluation of activated carbon adsorption for sewer odor control", Journal of the Water Pollution Control Federation, 51(5):1054 (1979).

4. J.M. Reid and M. McEvoy, "Monitoring sewer atmospheres for organic vapour", Journal of the Inst. of Water & Env. Mgmt. 1(2):161 (1987).
5. C. Matter-Muller, W.Gujer and W.Giger, "Transfer of volatile substances from water to atmosphere", Water Research, 15:1271 (1981).
6. R.L. Corsi, Volatile Organic Compound Emissions from Wastewater Collection Systems, Doctoral Dissertation, University of California, Davis, (1989).
7. D.J. O'Connor and W.E. Dobbins, "Mechanisms of reaeration in natural streams", Transactions, ASCE, 123:641 (1958).
8. T.E. Cadwallader and A.J. McDonnell, "A multivariate analysis of reaeration data", Water Research, 3: 731 (1969).
9. E.C. Tsioglou and L.A. Neal, "Tracer measurements of reaeration: II. Predicting the reaeration capacity of inland streams", Journal of the Water Pollution Control Federation, 48(12):2669 (1976).
10. J.D. Parkhurst and R.D. Pomeroy, "Oxygen absorption in streams", Journal of the Sanitary Engineering Division, ASCE, 98:101 (1972).
11. N.A. Jensen and T. Hvitved-Jacobsen, "Method of measurement of reaeration in gravity sewers using radiotracers", Journal of the Water Pollution Control Federation, 63(5):758 (1991).
12. R.L. Corsi et al., "Volatile and semi-volatile organic compound emissions from sewer drop structures", Proceedings of the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, 1992.

ACKNOWLEDGEMENTS

This work was supported by funds provided by the Ontario Ministry of the Environment (MOE). The authors would like to thank our MOE project liaison officer, Rob Paine, and all staff members from the Wastewater Technology Center, and the Metropolitan Works Department of Toronto who willingly participated in this research. Thanks also go out to Sandra Ausma and Perry Martos for their valuable time and efforts.

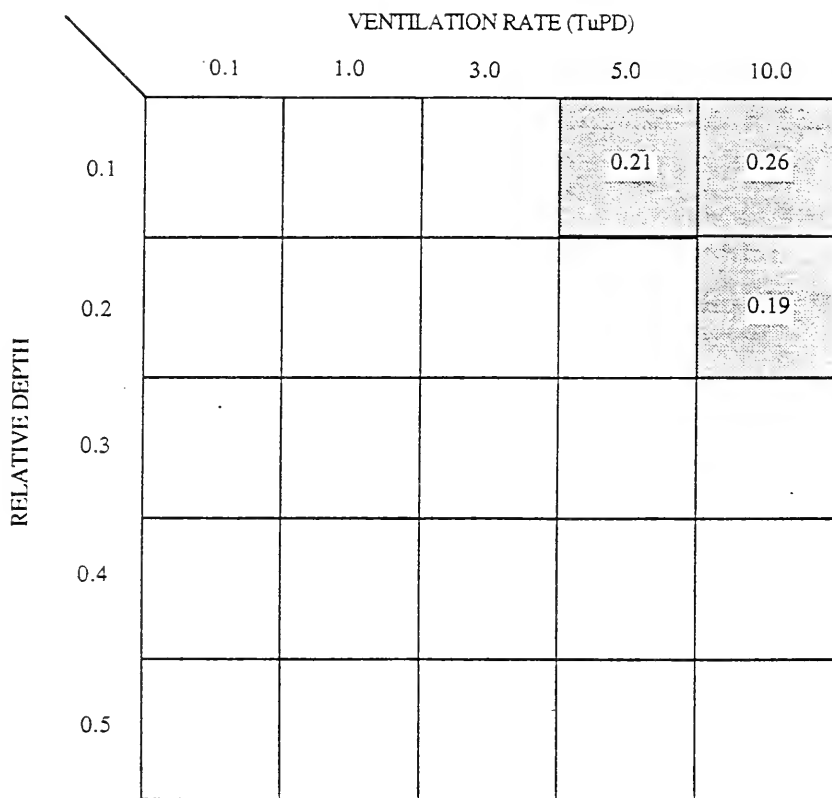


FIGURE 1. MATES sample frequency array.

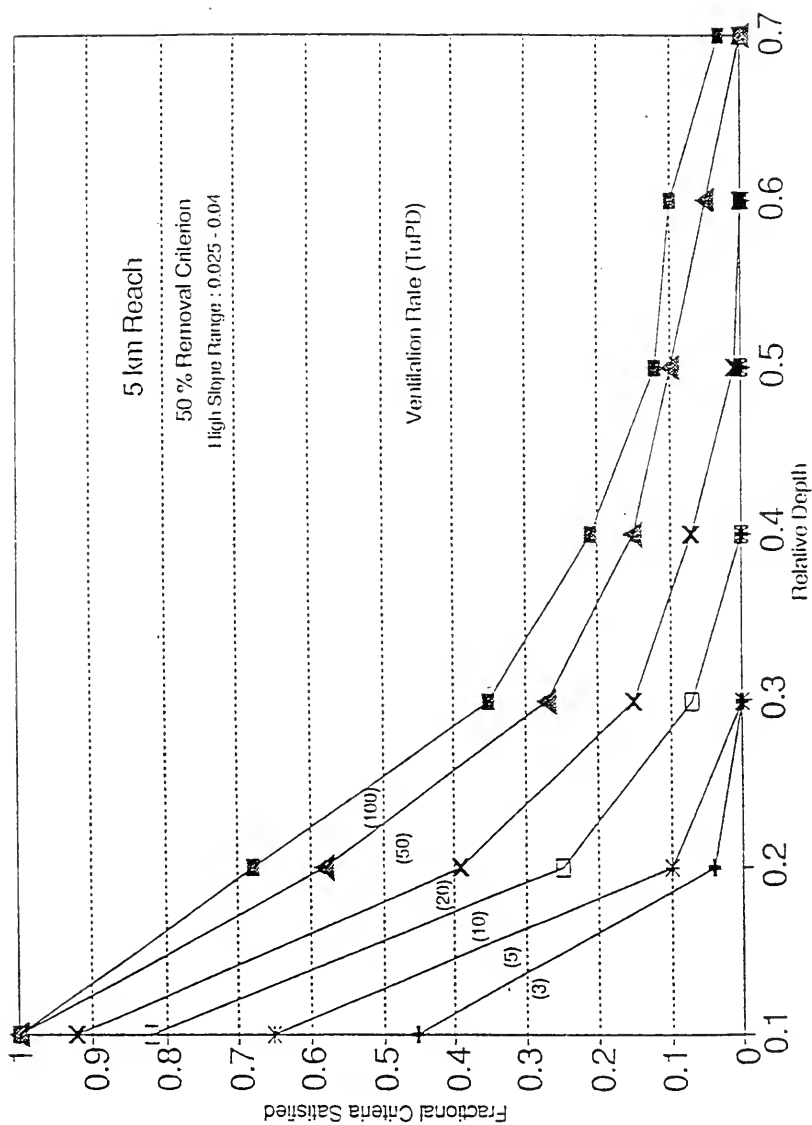


FIGURE 2. Fraction of cases in which 50% removal criterion was satisfied
(relative depth and ventilation rate)

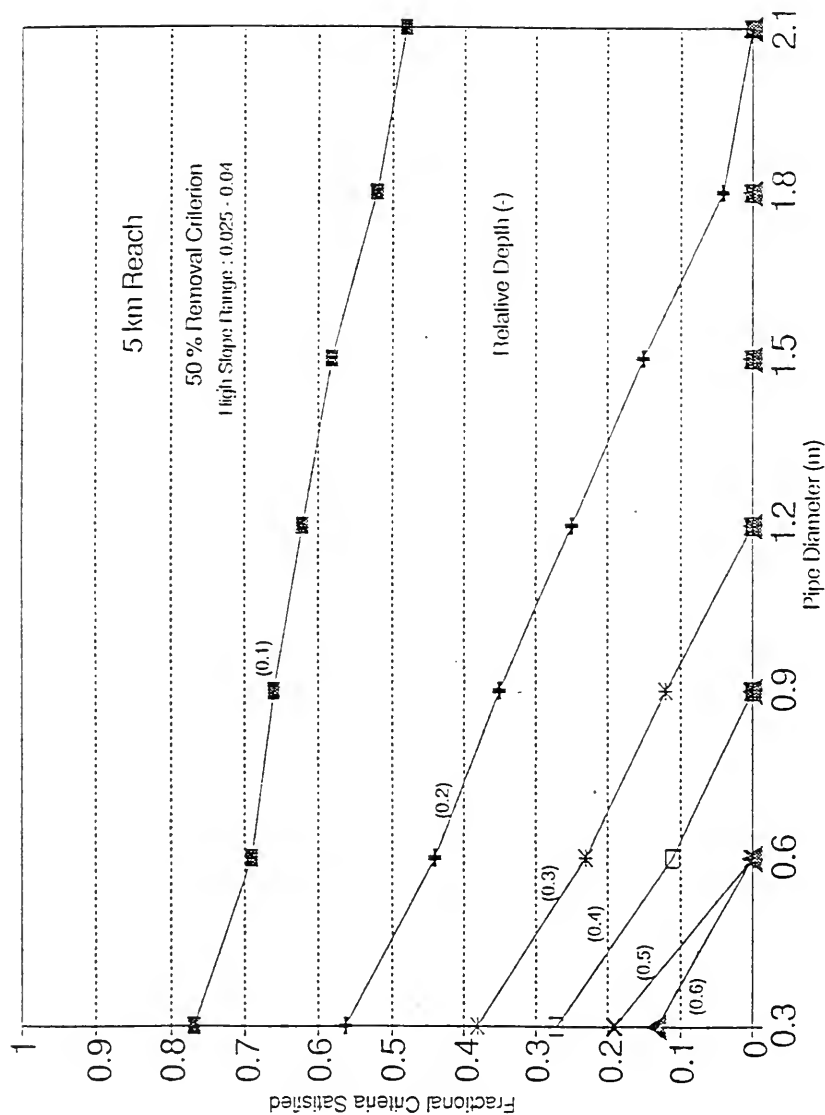


FIGURE 3. Fraction of cases in which 50% removal criterion was satisfied (relative depth and pipe diameter).

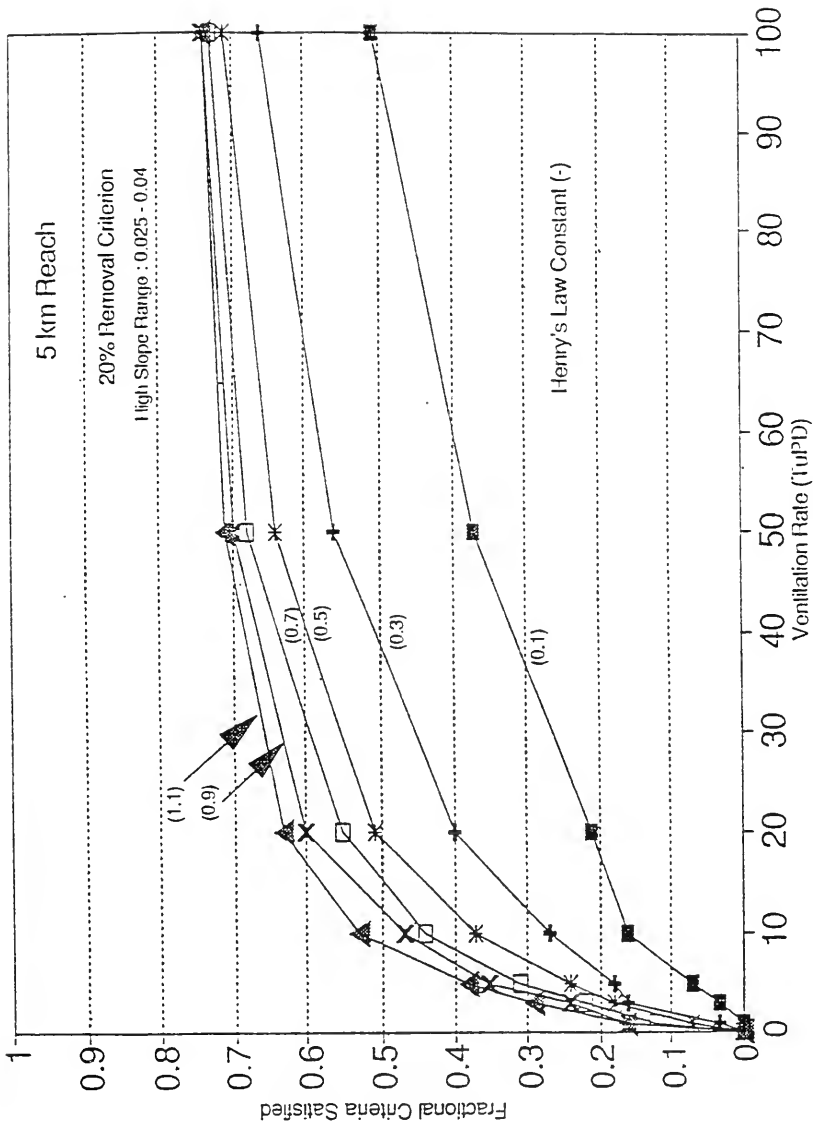


FIGURE 4. Fraction of cases in which 20% removal criterion was satisfied (Ventilation rate and Henry's law constant)



